U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-267 284

Treatment of Metal Finishing Wastes by Sulfide Precipitation

Metal Finishers' Foundation, Upper Montclair, N J

Prepared for

Industrial Environmental Research Lab -Cincinnati, Ohio Industrial Pollution Control Div

Feb 77

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-77-049	2.
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE TREATMENT OF METAL FINISHING WASTES BY SULFIDE PRECIPITATION	5. REPORT DATE February 1977 issuing date 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Richard M. Schlauch and Arthur C. Epstein of The Permutit Company	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Permutit Company, Permutit Research and Development Center, Princeton, New Jersey 08540 for The Metal Finishers' Foundation	10. PROGRAM ELEMENT NO. 1BB610 11. CONTRACT/GRANT NO. Grant No. R802924
12. SPONSORING AGENCY NAME AND ADDRESS Industrial Environmental Research Laboratory - Cin., OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED Final 14. SPONSORING AGENCY CODE EPA/600/12
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

This project involved precipitating heavy metals normally present in metal finishing wastewaters by a novel process which employs ferrous sulfide addition (Sulfex), as well as by conventional treatment using calcium hydroxide for comparison purposes. These studies consisted of laboratory jar tests and bench scale tests to determine the chemical and physical requirements for the precipitation of the heavy metals and the subsequent dewatering of the resulting sludges. Following the laboratory tests, pilot plant tests were made to confirm the validity of the laboratory test results and provide realistic operating data. As a result, it was demonstrated that Sulfex is a technically viable process that is superior to conventional hydroxide precipitation for removal of copper, cadmium, nickel, and zinc from a given influent. And, when operated in the pH 8-9.0 range, the Sulfex process will remove total chromium to a concentration which is less than or equal to that from a conventional hydroxide precipitation process. Hexavalent chromium can be removed by Sulfex in a one-step operation. The effluent quality from either process is dependent on the type and concentration of complexing agents present in the influent.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Industrial wastes, wastewater, waste treatment, metal finishing*, operating costs, precipitation*, ferrous sulfide* sludge disposal	Sulfide precipitation*, hydroxide precipitation* complexing agents, sludge dewatering	13B

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified 20. SECURITY CLASS *(This page)* Unclassified	21. NO. OF PAGES 89 22. PRICE PC A05-A01

EPA Form 2220-1 (9-73)

U.S. GOVERNMENT PRINTING OFFICE: 1977—757-056/5568

PB 267 284

EPA-600/2-77-049
February 1977

Environmental Protection Technology Series

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/2-77-049
February 1977

TREATMENT OF METAL FINISHING WASTES BY SULFIDE PRECIPITATION

by

Richard M. Schlauch
and
Arthur C. Epstein
The Permutit Company
Permutit Research and Development Center
Princeton, New Jersey 08540

For

Metal Finishers' Foundation
Upper Montclair, New Jersey 07043

Grant No. R802924

Project Officer

John Ciancia
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

ia

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory - Cincinnati, U. S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

The project was undertaken to demonstrate that ferrous sulfide treatment is a more effective process than conventional hydroxide treatment for heavy metal removal. In particular, the studies were aimed at treating metal finishing wastewaters that are difficult to treat with present-day standards by conventional treatment methods. The information contained in this report will be of value to EPA and to the industry itself. Within EPA's R&D program, the information will be used as part of a continuing program to develop and evaluate advanced precipitation methods for removal of heavy metals from industrial waste discharges. Besides its direct application to metal finishing wastes, this technology may find application in the control of heavy metals from effluents generated by a host of other industries. For further information concerning this subject, the Industrial Pollution Control Division should be contacted.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

This project involved precipitating heavy metals normally present in metal finishing wastewaters by a novel process which employs ferrous sulfide addition (Sulfex), as well as by conventional treatment using calcium hydroxide for comparison purposes. These studies consisted of laboratory jar tests and bench scale tests to determine the chemical and physical requirements for the precipitation of the heavy metals and the subsequent dewatering of the resulting sludges. Following the laboratory tests, pilot plant tests were made to confirm the validity of the laboratory test results and provide realistic operating data.

As a result, it was demonstrated that Sulfex is a technically viable process that is superior to conventional hydroxide precipitation for removal of copper, cadmium, nickel, and zinc from a given influent. And, when operated in the pH 8-9.0 range, the Sulfex process will remove total chromium to a concentration which is less than or equal to that from a conventional hydroxide precipitation process. Hexavalent chromium can be removed by Sulfex in a one-step operation. The effluent quality from either process is dependent on the type and concentration of complexing agents present in the influent.

This report was submitted in fulfillment of Grant No. R802924 by Metal Finishers' Foundation under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period April 1, 1974 to April 24, 1975 and work was completed as of May 2, 1975.

CONTENTS

		Page
Foreword		iii
Abstract		iv
List of Figures		vi
List of Tables		vii
List of Abbreviations and Symbols		viii
Acknowledgements		x
I	Introduction	1
II	Conclusions	9
III	Recommendations	11
IV	Laboratory Tests	12
V	Pilot Plant Tests	26
VI	Sludge Dewatering Tests	59
VII	Cost Estimates	62
VIII	References	75

LIST OF FIGURES

Number		Page
1	FeS dosage, sludge blanket concentration and mixing time vs. complexed copper removal	17
2	$Ca(OH)_2$ dosage, sludge blanket concentration and pH vs. complexed copper removal	19
3	Demonstration test pilot plant flow plan	27
4	Pilot plant package precipitator with chevron settlers	28
5	Mixing zone solids concentration vs. residual copper value for complexed Cu influent	34
6	Effluent pH value vs. effluent copper and iron concentration for complexed Cu influent..	39
7	Precipitator operating data for removal of complexed copper	43
8	Precipitator operating results for removal of complexed copper	44
9	Precipitator operating data for removal of complexed Cu, Cd, Cr, Ni, and Zn	53
10	Precipitator operating results for removal of complexed Cu, Cd, Cr, Ni, and Zn	54
11	Forty gpm Sulfex plant for combined removal of Cr^{+6}, Zn, Cu, Cd, Ni, and Fe	74

LIST OF TABLES

Number		Page
1	Common Complexing Agents Used in the Metal Finishing Industry	2
2	Solubility of Sulfides	6
3	Simulated Plating Waste Compositions	14
4	Sulfex Jar Test Results of Metal Removal With and Without Complexing Agents Present	20, 21
5	Jar Test Results Showing Influence of Complexing Agent Concentration on Metal Removal Comparing Hydroxide vs. Sulfex	23, 24
6	Pilot Plant Effluent Residuals for Copper and Iron at Different Operating Parameter Levels	33
7	Copper Removal in Various Stages of the Precipitator	36
8	Sludge Composition from Various Precipitator Zones	41
9	Effluent Metal Residuals from Precipitator Tests with Cu, Cd, Cr(III), Ni, and Zn in Influent	51
10	Chemical Costs of Hydroxide vs. Sulfex for Various Copper Concentrations	63
11	Chemical Costs of Hydroxide vs. Sulfex on Wastes Containing Mixtures of Common Heavy Metals	64

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

DCG	-- Permutit Dual Cell Gravity sludge dewatering unit
ft/sec	-- feet per second
gpm	-- gallons per minute
gpm/sqft	-- gallons per minute per square foot
I.D.	-- inside diameter
JTU	-- Jackson turbidity units
MFF	-- Metal Finishers' Foundation (of National Association)
mg/l	-- milligrams per liter
MRP	-- Permutit Multi Roller Press sludge drying unit
ppm	-- parts per million
rpm	-- revolutions per minute
X(FeS dose)	-- times theoretical FeS requirement

SYMBOLS

Ag_2S	-- silver sulfide
Bi_2S_3	-- bismuth sulfide
Ca	-- calcium
$Ca(OH)_2$	-- hydrated lime
Cd	-- cadmium
CdS	-- cadmium sulfide
CoS	-- cobalt sulfide
Cr	-- chromium
Cr^{+3}	-- trivalent chrome
Cr^{+6}	-- hexavalent chrome
$CrO_4^=$	-- chromate ion
$Cr(OH)_3$	-- chromic hydroxide
Cu	-- copper
CuS	-- cupric sulfide
EDTA	-- ethylene diamine tetraacetic acid
Fe	-- iron
Fe^{++}	-- ferrous iron
Fe^{+++}	-- ferric iron
$Fe(OH)_2$	-- ferrous hydroxide
$Fe(OH)_3$	-- ferric hydroxide
FeS	-- ferrous sulfide
$FeSO_4$	-- ferrous sulfate

SYMBOLS (continued)

HgS	-- mercuric sulfide
H_2S	-- hydrogen sulfide gas
H_2SO_4	-- sulfuric acid
K	-- potassium
MnS	-- manganous sulfide
Na	-- sodium
$NaHS$	-- sodium hydrosulfide
Na_2S	-- sodium sulfide
$Na_2S_2O_5$	-- sodium metabisulfite
NH_3	-- ammonia gas
Ni	-- nickel
NiS	-- nickelous sulfide
PbS	-- lead sulfide
S^o	-- sulfur (elemental)
$S^=$	-- sulfide ion
Zn	-- zinc
ZnS	-- zinc sulfide

ACKNOWLEDGMENTS

The authors gratefully acknowledge the cooperation and assistance of the Metal Finishers' Foundation, the sponsor of this project. Permutit performed this work under Metal Finishers' Foundation Subcontract for Research No. 74-1 entitled "Treatment of Metal Finishing Wastes by Sulfide Precipitation". The financial assistance provided by the sponsor was made possible under Grant No. R802924-01 from the Environmental Protection Agency. The advice and cooperation of Mr. E. Durkin, Vice President and Chairman of the Pollution Control Committee of MFF, Mr. P. Kovatis, Secretary of MFF, and Mr. J. Ciancia, former Chief of Industrial Pollution Control Branch, EPA, Edison, New Jersey are gratefully appreciated.

Acknowledgment is made to Dr. J. Anderson and Dr. C. Weiss, the co-inventors of the Sulfex process. Their varied contributions were necessary to the undertaking of this project. The proficient direction of Mr. W. A. Beach, the Program Manager, is also recognized. His guidance throughout the project is sincerely appreciated. Mr. C. Wroblewski, Engineering Technician, provided expertise in assembling and operating the pilot plant that greatly assisted in obtaining a smooth running project. His skillful control of the plant and attentive data and sample collection helped in achieving reliable evaluation of results. The help of Mr. R. Shuler, Mr. R. Freeman, and Mr. A. LaTourette in assembling and operating the pilot plant is also appreciated.

Mr. W. Schwoyer and Mr. S. Blair were responsible for the laboratory evaluation tests for sludge dewatering. Their recommendations and assistance in running the pilot plant dewatering equipment were also of great importance to the project.

We wish to express gratitude to Mrs. C. Glover and her analytical staff, Mr. T. Savonick and Mr. R. Irons, who performed all the analytical services for this project. This work involved time-consuming analytical procedures on hundreds of samples. Their cooperation and tolerance deserve special appreciation.

The advice of Dr. L. Luttinger and Mr. W. Malkin, the Project Consultants, was helpful in establishing the project objectives and evaluating the results. Additional consultation and reviewing of the final report by Mr. K. Quazza, Mr. M. Scott, and Mr. A. Mindler is also gratefully acknowledged.

SECTION I

INTRODUCTION

A. Hydroxide Precipitation

The function of waste treatment in metal finishing facilities is to reduce the metals, dirt, grease and oil to a level allowable for discharge to a receiving body of water. The contents of the waste dictate whether one step or more steps are needed. If cyanide and/or hexavalent chromium are present in the waste, they must be pretreated individually, and then recombined with the main waste stream for metal removal.

The common process for metal removal is the precipitation of the metallic hydroxides. The wastewater is treated with either lime or caustic to cause precipitation of the metal hydroxides. Since heavy metal hydroxides are gelatinous and difficult to flocculate, a coagulant or flocculant aid is usually used.

There are two basic objections to the hydroxide precipitation process. First, the solubilities of certain heavy metal hydroxides are sufficient as to allow excessive amounts of metal to remain in solution at normal pH discharge limits. An example of this is cadmium hydroxide, $Cd(OH)_2$, with a solubility ranging between 0.1 to 1.0 mg/l as Cd^{++}. Compare these numbers with many statutes* which prohibit discharges containing no more than 0.01 mg/l of cadmium. Second, in the presence of certain complexing agents, the precipitation of the metal ion is incomplete. The prevalence of these complexing agents in metal bearing waste treatment systems is often overlooked or unrecognized. This becomes increasingly true as industry turns, more frequently, to proprietary chemicals for their metal finishing formulations.

---

* Examples:
1. Montana State Department of Health and Environmental Sciences MAC 16-2.4 (10)-S14480 Water Quality Standards
2. Definition Regulation Missouri Clean Water Commission May 1974.

Some of the metal complexes are so stable that hydroxide precipitation is thermodynamically impossible to initiate even at a pH well above that normally permissible for discharge. In addition, the complexes are usually found in concentrations that are one or more orders of magnitude greater than the concentration of the metals. The mass action principle, therefore, enhances the stability of the complexes. A list of the common complexing agents, together with the operations that utilize them, is given in Table 1.

Table 1. COMMON COMPLEXING AGENTS USED IN THE METAL FINISHING INDUSTRY

Complexing Agent	Process
Phosphates	Alkaline Cleaners
E.D.T.A.	Electroless Plating Baths
Cyanides	Plating Baths
Tartrates	Electro and Electroless Baths
Ammonia	Metal Etchants

When in solution, complexing agents such as these prevent the complete precipitation of heavy metal hydroxides by competing with the hydroxyl ion for possession of the heavy metal, e.g.,

$$Zn(NH_3)_4^{++} + 2OH^- = Zn(OH)_2 + 4NH_{3\,(aq)} \qquad (1)$$

Equation (1) indicates that solutions which contain dissolved ammonia tend to drive the reaction to the left, thereby preventing removal of zinc as the hydroxide. Calculations show that for a solution containing 100 ppm of dissolved NH_3, at a pH of 8.0, nearly 3.0 ppm of Zn^{++} will remain unprecipitatd. All complexing agents will solubilize certain heavy metals in a fashion similar to that given in the above example.

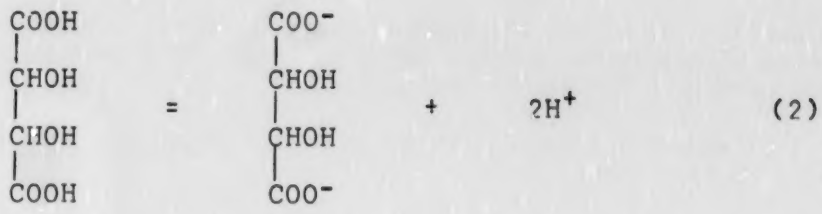
Another example[1] of a complexing agent encountered in electroplating is the tartrate ion which reacts with certain heavy metals to form metal-tartrate ion complexes, e.g.,

---

REFERENCES

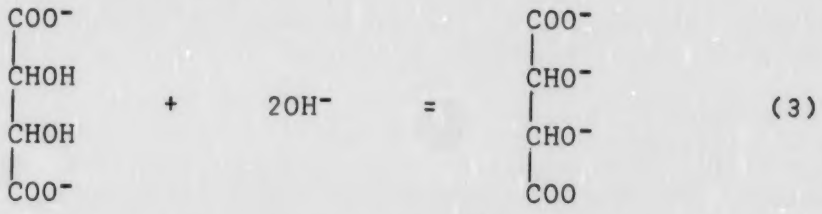
1. Fales, H. A. and F. Kenny. Inorganic Quantitative Analyses. New ed. Appleton Century Co., New York-London, p. 233, 1939.

1. In acidic solution



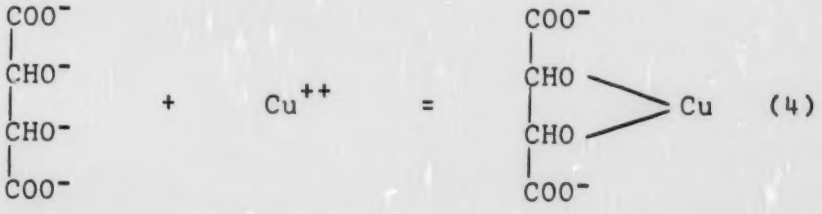
Tartaric Acid — Tartrate Ion (2)

2. In alkaline solution



Tartrate Ion — Complex-forming Tartrate Ion (3)

3. In presence of metal ion



Complex-forming Tartrate Ion — Cupri-tartrate Ion Complex (4)

The tartrate ion, therefore, increases its complex forming character with increasing pH value. In addition, with the increasing use of proprietary formulations containing various brighteners, wetting agents, etc. complexing agents of unknown composition can be introduced into plating wastewaters without the operator's knowledge.

B. Sulfide Precipitation

Realizing the need for a metal removal process effective in the presence of complexing agents, Permutit initiated a program to develop such a process. The effort was guided by the following requirements:

1. The process must be workable over a broad spectrum of waste compositions.

2. It should not require any specialized equipment or skills foreign to the customer.

A precipitation technique that satisfies these requirements has been developed. The technique involves an exchange of ions between the sulfide of an added heavy metal and the ligand of the pollutant ion(s). Hence, the name "Sulfex". Sulfide precipitation, by forming extremely insoluble species, overcomes both the problem of limited hydroxide insolubility and the problem of complexing agents.

The question that immediately arises is, "Why hasn't sulfide precipitation been universally adopted as the treatment method of choice?" Two basic reasons follow: Sulfide systems have earned reputations for generating noxious hydrogen sulfide gas and forming colloidal and otherwise difficulty settleable precipitates. The "Sulfex" process overcomes these objections and provides discharges of such purity that the user can generally satisfy the most stringent clean water codes.

How, then, does the "Sulfex" process differ from pH controlled addition of H_2S or Na_2S? In simplest terms, the "Sulfex" process uses a source of sulfide ion, a sparingly soluble but non-toxic heavy metal sulfide, such as FeS. Its reaction with Cu^{++} ions in a solution containing EDTA as, for example, the rinses following an electroless copper plating bath takes place as follows:

$$CuEDTA^{-2} + FeS_{(s)} = CuS_{(s)} + FeEDTA^{-2} \qquad (5)$$

In contrast, the reaction using a soluble source of sulfide ions such as Na_2S or NaHS occurs as follows:

$$CuEDTA^{-2} + S^{-2} = CuS_{(s)} + EDTA^{=} \qquad (6)$$

Both processes are effective in breaking up the complex and precipitating copper sulfide. However, because FeS has a very low water solubility, its tendency to react with water, and thereby generate H_2S gas, is low as compared with an equivalent amount of a very soluble sulfide, i.e. the reaction

$$FeS_{(s)} + 2H_2O = Fe^{++} + 2\ OH^- + H_2S_{(g)} \qquad (7)$$

does not proceed as completely as does

$$Na^+ + HS^- + H_2O = OH^- + H_2S_{(g)} + Na^+ \qquad (8)$$

Calculations show that for solutions containing 20 ppm of sulfide, added in one case as NaHS and in the other case as FeS, the vapor over the solution contains, in the former case, 0.8 ppm of H_2S but in the latter case only about 0.003 ppm. This last number is very close to the minimum value detectable by smell, viz. 0.002 ppm as reported in the Eighth Edition of the Merck Index.

However, it is more important to recognize that, in the case of reaction (7), the amount of FeS added to the solution has no effect on the amount of H_2S in the air above it. This is true because once you have saturated a solution with an insoluble substance, like FeS, no more can dissolve. However, in the case of reaction (8), any increase in the amount of sulfide that would occur with poorly controlled addition of a soluble sulfide leads to an increase in the concentration of H_2S in the air. These are extremely important concepts in the design of the chemical metering systems and from the point of view of operating comfort and safety. We can sum up by saying that the "Sulfex" system is, therefore, self-regulating with respect to the sulfide content of the solution. No more sulfide dissolves than is required to precipitate the toxic ions. Systems using soluble sulfides as precipitating agents do not have this advantage.

In theory, any metal sulfide more soluble than the pollutant sulfide can be used as a precipitant providing the equilibrium is such as to give residual pollutant levels in accord with existing legal specifications. This point can be better understood from examination of Table 2 which is a listing of the common metal sulfides arranged in order of decreasing solubility.

In order to maximize the driving force for the precipitation, one naturally chooses as a precipitant a sulfide having the highest possible equilibrium sulfide ion concentration. If, for example, one had a waste containing cadmium, copper and mercury, one could choose as a precipitant any sulfide from PbS or MnS. However, one would not, for example, select ZnS as a precipitant for Ni^{++} because their nearly equivalent equilibrium sulfide ion concentrations would not provide sufficient driving force for the precipitation of NiS.

In practice, ferrous sulfide is the precipitant normally chosen for obvious reasons. It has a comparatively high solubility; it can be prepared inexpensively; and iron is, generally, non-toxic.

Table 2. SOLUBILITY OF SULFIDES

Metal Sulfide	Ksp (18 to 25°C)	Sulfide Concentration (Moles/l)
MnS	1.4×10^{-15}*	3.74×10^{-8}
FeS	3.7×10^{-19}*	6.1×10^{-10}
ZnS	1.2×10^{-23}*	3.46×10^{-12}
NiS	1.4×10^{-24}*	1.18×10^{-12}
SnS	1.0×10^{-25}**	3.16×10^{-13}
CoS	3.0×10^{-26}*	1.73×10^{-13}
PbS	3.4×10^{-28}*	1.84×10^{-14}
CdS	3.6×10^{-29}*	6.0×10^{-15}
Ag_2S	1.6×10^{-49}*	3.4×10^{-17}
Bi_2S_3	1.0×10^{-97}**	4.8×10^{-20}
CuS	8.5×10^{-45}*	9.2×10^{-23}
HgS	2.0×10^{-49}*	4.5×10^{-25}

REFERENCES

* 2. Handbook of Chemistry and Physics. 50th Ed., Robert C. Weast, Ed. The Chemical Rubber Company 1969, p. B252

** 3. Handbook of Analytical Chemistry. Louis Meites, Ed. McGraw-Hill, Inc. 1963, pp. 1-15, 1-19.

The program used to demonstrate the superiority of ferrous sulfide, as compared to lime, for removal of complexed and uncomplexed heavy metals from solution was as follows:

A. Phase I - Precipitation and Filtration Studies

1. Section 1 - Laboratory Tests (jar tests)
2. Section 2 - Assembly and piping of the pilot plant
3. Section 3 - Precipitator tests
4. Section 4 - Optimization tests
5. Section 5 - Analytical work

B. Phase II - DCG (Sludge Dewatering) Tests

1. Section 1 - Laboratory tests
2. Section 2 - Full scale DCG tests
3. Section 3 - MRP tests
4. Section 4 - Analytical work

C. Phase III - Final Report

This plan was based on testing only one simulated wastewater: an electroless copper plating waste containing 20 mg/l of copper complexed by EDTA and Rochelle salt*. However, Permutit in conjunction with the MFF and EPA increased the scope of work to include:

1. An influent containing 50-80 mg/l of dissolved iron in addition to the 20 mg/l of complexed copper.

2. An influent containing only 5 mg/l of complexed copper.

3. An influent containing 60-90 mg/l of complexed copper.

4. An influent containing five metals (copper, cadmium, chrome, nickel, and zinc) complexed with EDTA and Rochelle salt. The concentration of each metal was 4 mg/l.

5. An influent containing five metals (copper, cadmium, chrome, nickel, and zinc) complexed only with Rochelle salt.

6. Large scale tests of hydroxide precipitation using lime and influent 5.

---

* Rochelle salt is sodium potassium tartrate.

For reasons of effectiveness, availability, and economy, the ferrous sulfide is not added as ferrous sulfide but instead is freshly precipitated by reacting an iron salt with a soluble sulfide such as sodium sulfide, sodium hydrosulfide, or hydrogen sulfide. These soluble sulfides are used effectively in the process, to form FeS, if a source of alkali such as lime or sodium hydroxide is simultaneously added to maintain the pH at a value higher than 7.0 in order to prevent evolution of hydrogen sulfide gas.

Another advantage of the Sulfex process is its abaility to remove hexavalent chromium in one step as opposed to the typical two-step process used with hydroxide precipitation.

$$CrO_4^{=} + 4H_2O + FeS_{(s)} = S^{o}_{(s)} + Fe(OH)_{3(s)} + Cr(OH)_{3(s)} + 2OH^{-} \quad (9)$$

SECTION II

CONCLUSIONS

As a result of the laboratory jar test studies and pilot plant demonstration tests, it is concluded that:

A. The Sulfex process is a technically viable process.

B. When treating the same influent, the Sulfex process obtains lower residuals of copper, cadmium, nickel, and zinc than can be obtained with the hydroxide process.

C. At the same pH value, the Sulfex process removes chromium to a concentration which is less than or equal to that from a hydroxide precipitation process.

D. The reduction of hexavalent chrome to trivalent chrome can be performed by Sulfex in one step at slightly alkaline pH values (i.e. pH 8.0 to 9.0). For this reason, Sulfex does not require segregation of chrome containing wastes from other heavy metal containing wastes.

E. Satisfactory effluent quality is usually obtained with the Sulfex Process within the 8.5 to 9.0 pH range which is within the 6.0 to 9.5 pH range permitted by the EPA for discharge. The hydroxide process is often not satisfactory in this pH range and sometimes not effective even if raised above pH 10 and readjusted within permitted discharge limit.

F. The effluent quality from either process is dependent on the type of complexing agents present in the effluent. Examples of the effluent quality obtained by the Sulfex process with 4 mg/l of each metal in the effluent are:

   1. For metals complexed with high concentrations of EDTA and Rochelle salt.

copper	- 0.2 mg/l
zinc and cadmium	- 1.0 mg/l
nickel and chrome	- 3.0 mg/l

2. For metals complexed with high concentrations of Rochelle salt only.

cadmium	-	<0.01 mg/l
copper	-	0.01 mg/l
zinc	-	0.03 mg/l
nickel	-	0.4 mg/l
total chrome	-	3 mg/l

3. For metals with no complexing agents

cadmium	-	<0.01 mg/l
copper	-	0.01 mg/l
zinc	-	0.01 mg/l
nickel	-	<0.05 mg/l
total chrome	-	<0.05 mg/l

G. Using the Sulfex process, the removal of a particular heavy metal is more effective when it is in a solution containing other heavy metals than when it is the only metal in solution.

H. The Sulfex process can be applied in Precipitators (and similar devices) at surface rates up to 2.0 gpm/sq.ft. when tube settlers are used.

I. The required dosage of ferrous sulfide reactant is dependent upon the type of waste being treated. It should normally vary from about 1.5 times theoretical requirement for wastes with no complexing agents to 3 or more times theoretical for wastes containing complexing agents.

J. The concentration of settleable ferrous sulfide solids in the mixing zone, the pH of the process, and use of certain polyelectrolytes are important to obtaining satisfactory results in the Sulfex process.

K. To treat many common plating wastes (without strong complexing agents) containing an average of about 20 mg/l total heavy metals, the operating cost of Sulfex compares favorably with that of conventional hydroxide precipitation.

L. It may be more economically desirable to pretreat wastes containing high concentrations of dissolved heavy metals (i.e., a total heavy metal concentration greater than 50 mg/l) by hydroxide before polishing with Sulfex.

M. Conventional dewatering methods can dewater the sludge from the Sulfex process to a bladeable solid suitable for disposal.

SECTION III

RECOMMENDATIONS

It has been demonstrated in these tests that Sulfex treats various heavy metal influent compositions to lower effluent metal concentrations than conventional hydroxide precipitation processes. The operational costs for Sulfex appear to be reasonably practical when treating most plating waste compositions containing up to a total of about 50 mg/l of dissolved heavy metals. However, further test work should be performed on actual plating wastes both in the laboratory and on-site in the field. Such tests are necessary to evaluate the effectiveness of Sulfex under conditions that cannot be simulated. In addition, the economics of Sulfex is best evaluated under the actual wastewater conditions existing at the plating operation.

SECTION IV

LABORATORY TESTS

A. Composition of Plating Wastes

There were several different compositions of simulated plating wastes used during the course of these studies. The initial work used a waste which would be extremely difficult to treat by conventional hydroxide precipitation. The composition of the waste is shown in Column I of Table 3. The simulated waste solution was prepared by diluting a published[4] electroless copper plating solution formula 444.4 times with tap water. This dilution was used in order to obtain a waste solution containing 20 mg/l copper ion. This copper concentration is assumed to be representative of the concentration of all the heavy metal ions, except iron, found in waste effluents from plating processes.

This waste is assumed to be typical of the waste from many electroless copper plating facilities. Although it is not typical of the waste from the majority of metal finishing plants, it was selected because of the high concentrations of a strong complexing agent (EDTA) and a moderately strong complexing agent (Rochelle salt). Such wastes are not satisfactorily treated by conventional hydroxide precipitation methods. The satisfactory treatment of this waste by Sulfex would, therefore, show superiority of Sulfex over the hydroxide method.

The fact that it is particularly difficult to remove dissolved copper from this waste by hydroxide precipitation is indicated by its already high pH (11.2) without copper precipitate being formed. The pH of the concentrated plating solution before dilution was 13.7 and 13.8, and no precipitation of copper was evident even after several months of standing. This is further evidence that this solution of strongly complexed copper is very resistant to complete copper removal by hydroxide precipitation processes.

REFERENCES

4. Metal Finishing Guidebook and Directory for 1970. Nathaniel Hall, ed., Palmer H. Langdon, pub. 1970 p. 473.

Because of a substantial cost increase for tartrates, the composition of the waste used for the precipitator tests was modified by the reduction in concentration of the Rochelle salt to one-third of its original concentration (see Column II, Table 3). Since the concentration of the strong complexing agent was not changed, the results were not expected to be significantly different from those obtained in jar tests.

During the program, the EPA and MFF requested we perform tests with other metals which were of interest. These metals were copper, cadmium, chromium, nickel, and zinc. It was pointed out that the majority of the waste streams they were interested in would not contain EDTA or Rochelle salt. In fact, there would only be low concentrations (if any) of complexing agents. However, in order to study the effects of these complexing agents on the heavy metals, either both, one, or neither of them were included in jar tests with simulated five metal wastes. These formulations are shown in Columns III, IV, and V, respectively, of Table 3. The effect of each of these complexing agents on the five heavy metals was then observed.

B. Parameters Studied in the Jar Tests

1. Description of Jar Tests

The jar tests were performed on 4 liter and 0.5 liter samples of the simulated plating wastes. When the chemical reactants were added (i.e. FeS, $Ca(OH)_2$, etc.), the sample was mixed rapidly (100 rpm) for periods of 30 to 60 seconds. This step simulates the fast mix operation of a coagulation system. The FeS was added to the jar tests samples by either of two different methods: (1) separate solutions of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and sodium sulfide ($Na_2S \cdot 9H_2O$) were added directly to the rapidly mixing heavy metal waste solution or (2) the ferrous sulfate solution was slowly added to the rapidly mixing sodium sulfide solution, forming a concentrated slurry of FeS that was then added to the rapidly mixing heavy metal waste solution. These tests confirmed previous studies which showed the first method was unacceptable because it promoted colloidal heavy metal sulfide suspensions, whereas the second method promotes larger FeS particles and clearer supernatants.

Table 3. SIMULATED PLATING WASTE COMPOSITIONS

Chemical	I ppm	II ppm	III ppm	IV ppm	V ppm
(1) Rochelle salts (as K-Na Tartrates)	383	127	126.9	126.9	-
(2) EDTA as (Na_4EDTA)	45	45	45	-	-
(3) Sodium hydroxide (as NaOH)	112.5	10	19.9	19.9	-
(4) Soda Ash (as Na_2CO_3)	67.5	67.5	-	-	-
(5) Copper Sulfate (as $CuSO_4 \cdot 5H_2O$)	78.5	78.5	15.75	15.75	15.75
Copper (as Cu^{++})	20	20	4.0	4.0	4.0
(6) Cadmium Chloride (as 80% $CdCl_2 \cdot 2\frac{1}{2}H_2O$)	-	-	10.17	10.17	10.17
Cadmium (as Cd^{++})	-	-	4.0	4.0	4.0
(7) Chromic Acid (as CrO_3) + 4.5 mg/l H_2SO_4 + 22 mg/l $Na_2S_2O_5$) (to reduce Cr^{+6} to Cr^{+3})	-	-	7.7	7.7	7.7
Chrome (as Cr^{+++})	-	-	4.0	4.0	4.0
(8) Nickelous Nitrate (as $Ni(NO_3) \cdot 6H_2O$)	-	-	19.8	19.8	19.8
Nickel (as Ni^{++})	-	-	4.0	4.0	4.0
(9) Zinc Chloride (as $ZnCl_2$)	-	-	8.6	8.6	8.6
Zinc (as Zn^{++})	-	-	4.0	4.0	4.0
(10) pH	11.2	8.8-9.0	7-7.5	6.8	~6.0
(11) Suspended Solids	less than 1.0	-	-	-	-

The rapid mix period was followed by slow speed mixing (25 to 30 rpm) lasting from 10 to 60 minutes. The samples were then allowed to settle without mixing for periods of 1 to 30 minutes. The amount of time allowed for settling depended on whether precipitate settling rates were being measured or the sample was only being evaluated for dissolved heavy metal reduction after settling and filtering.

To determine the effect of sludge blanket contact, previously settled solids formed in the larger volume jar tests were added to the mixing stage of the smaller volume jar tests. To measure the total concentration of dissolved heavy metals, iron, calcium, etc. remaining in a sample after settling, the supernatant was immediately filtered through a 0.45 micron Millipore filter to remove colloidal constituents before the chemical analyses were made. Before the analyses, the samples were acidified to a pH less than 2.0 in order to prevent post-precipitation of heavy metals. All analyses were made by atomic absorption spectrophotometry.

2. Jar Tests on Waste Containing Complexed Copper

The objective of these jar tests was to determine the effects of various operating parameters on precipitating, coagulating, and settling the copper from solution. These operating parameters would then be optimized during Precipitator tests. It was assumed the effect of these operating parameters on copper removal would be similar for the removal of several other heavy metals. The target for residual copper ion in a filtered effluent was less than or equal to 0.1 mg/l as Cu^{++}. This is at least ten times lower than is usually obtained from the hydroxide process (1.0-1.5 mg/l). The parameters studied were:

a. Ferrous sulfide (FeS) dosage
b. FeS sludge blanket concentration
c. FeS sludge blanket solids contact time with the liquid waste (i.e. mixing time)
d. Use of coagulant aids for promoting faster clarification when FeS is used as the reactant

   (1) Type of coagulant aids required
   (2) Concentration of coagulant aids required
   (3) Addition time of coagulant aids

e. Use of lime, $Ca(OH)_2$, as the reactant at various pH values and sludge blanket concentrations

3. Results of Jar Tests on Complexed Copper Waste

The jar tests show that increasing FeS dosage, increasing mixing time (i.e. liquid-solids contact time), and increasing sludge blanket concentration each have individual positive influences on copper removal. Combining all of these "positive" parameters is beneficial, but the most important single parameter appeared to be the sludge blanket solids concentration. The sludge blanket forms as FeS, CuS, and other possible precipitates, build up and concentrate in the mixing and settling zones of the Precipitator.

a. The jar tests indicate that for each equivalent of complexed copper between two and three equivalents of FeS give excellent copper removal when a concentrated sludge blanket is maintained. The pH during these jar tests was maintained in the 7.0 to 8.0 pH range. Figure 1 shows the effect of increased FeS dosage on copper removal as a function of sludge blanket concentration. The best results are obtained when the sludge blanket is the most concentrated (5000 mg/l suspended solids). Copper removal is improved as the FeS dosage is increased in the presence of a sludge blanket. It is also seen that with no sludge blanket, the removal of copper is improved with increasing dosages of FeS.

b. Figure 1 demonstrates that a sludge blanket concentration of several thousand mg/l suspended solids (as FeS) should be maintained to obtain essentially complete copper removal.

c. Figure 1 shows that increasing the mixing time from 10 minutes to 60 minutes with a dilute sludge blanket gives only a modest improvement in copper removal. However, with an adequate FeS concentration continuously supplied and with a sludge blanket sufficiently concentrated with FeS, a liquid-solids contact period of 45 to 60 minutes is sufficient to reduce the residual copper to the desired level.

d. Results of the jar tests indicate that a coagulant aid is important to maintaining a concentrated sludge blanket and a clear effluent. The presence of metal complexing agents apparently prevented the common inorganic coagulants such as aluminum sulfate and ferric sulfate from flocculating well in the simulated waste sample. It is found that 1 to 5 mg/l of a cationic natural gum derivative polymer is very effective in maintaining a concentrated sludge blanket. Some synthetic cationic polyelectrolytes also displayed effectiveness in coagulating the colloidal

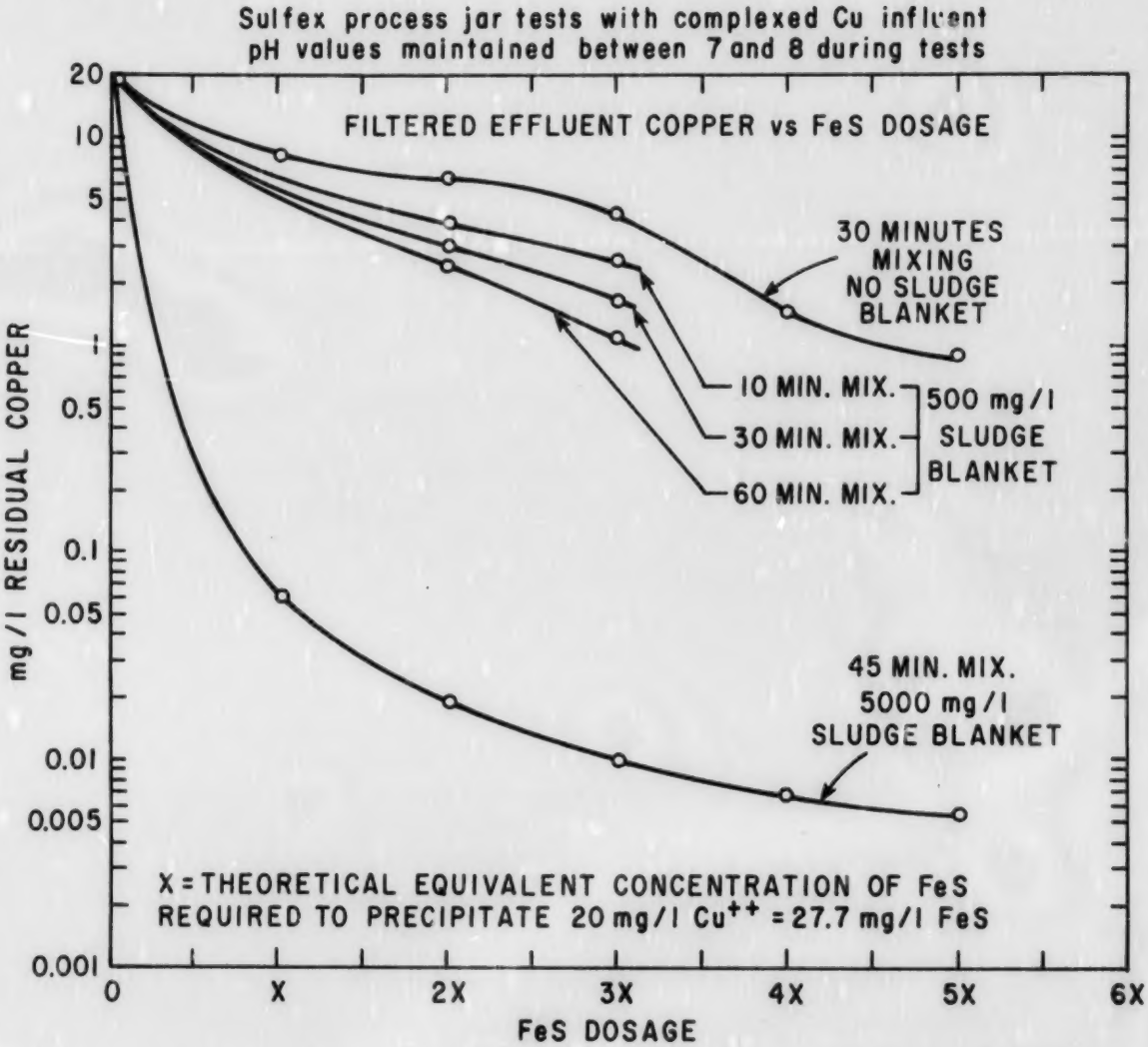


Figure I. Influence of FeS dosage, sludge blanket concentration and mixing time on copper removal.

metal sulfide particles. However, during extended mixing periods, the sludge appears to be more resistant to mechanical breakdown into colloidal particles when coagulated with the natural gum polymer than with the synthetic polyelectrolyte. The cationic polyelectrolytes are most beneficial when the polymer solution is added to the mixing stage a few minutes after the addition of the other chemicals.

A series of jar tests were performed to evaluate the copper removal capability of the hydroxide process when treating a strongly complexed copper waste. The hydroxide was added as lime. The results of these tests are shown in Figure 2. For these tests, the simulated copper plating waste at pH 11.2 was first acidified to pH 4.5 for 5 minutes in an attempt to destroy the copper complexes. Then, lime, in various dosages, was added to the copper plating waste which was mixed, settled, filtered and analyzed by the same procedure as used in the Sulfex tests. Figure 2 shows the pH of the solution must be raised to 12 in order to reduce the copper residual to 4 mg/l. Figure 2 also shows that lime in massive doses is required to achieve a pH of 12.

4. Jar Tests on Wastes Containing Copper, Cadmium, Chromium, Nickel, and Zinc

In addition to copper, the removal of cadmium, chromium, nickel, and zinc was studied. The influent concentration of each metal was 4 mg/l. In one series of Sulfex jar tests, the five metals were in a mixed solution. In another series, the five metals were studied as individual solutions. Parameters which were studied included the presence versus the absence of complexing agents, the influence of pH, and the ferrous sulfide dosage. The results of both series of jar tests (i.e. individual versus mixed ions) are shown in Table 4. The conclusions from these Sulfex jar tests are:

a. The removal of a particular metal is usually better when it is in a solution containing other heavy metals then when it is the only metal in solution.

b. The presence of high concentrations of Rochelle salt and EDTA give higher residuals for nickel and chrome than for copper, cadmium, and zinc.

c. Increasing the pH reduces the residual metal concentration for all five metals whether complexing agents are present or not. The iron which is introduced into the solution as ferrous sulfide also has its effluent concentration reduced by increasing the pH.

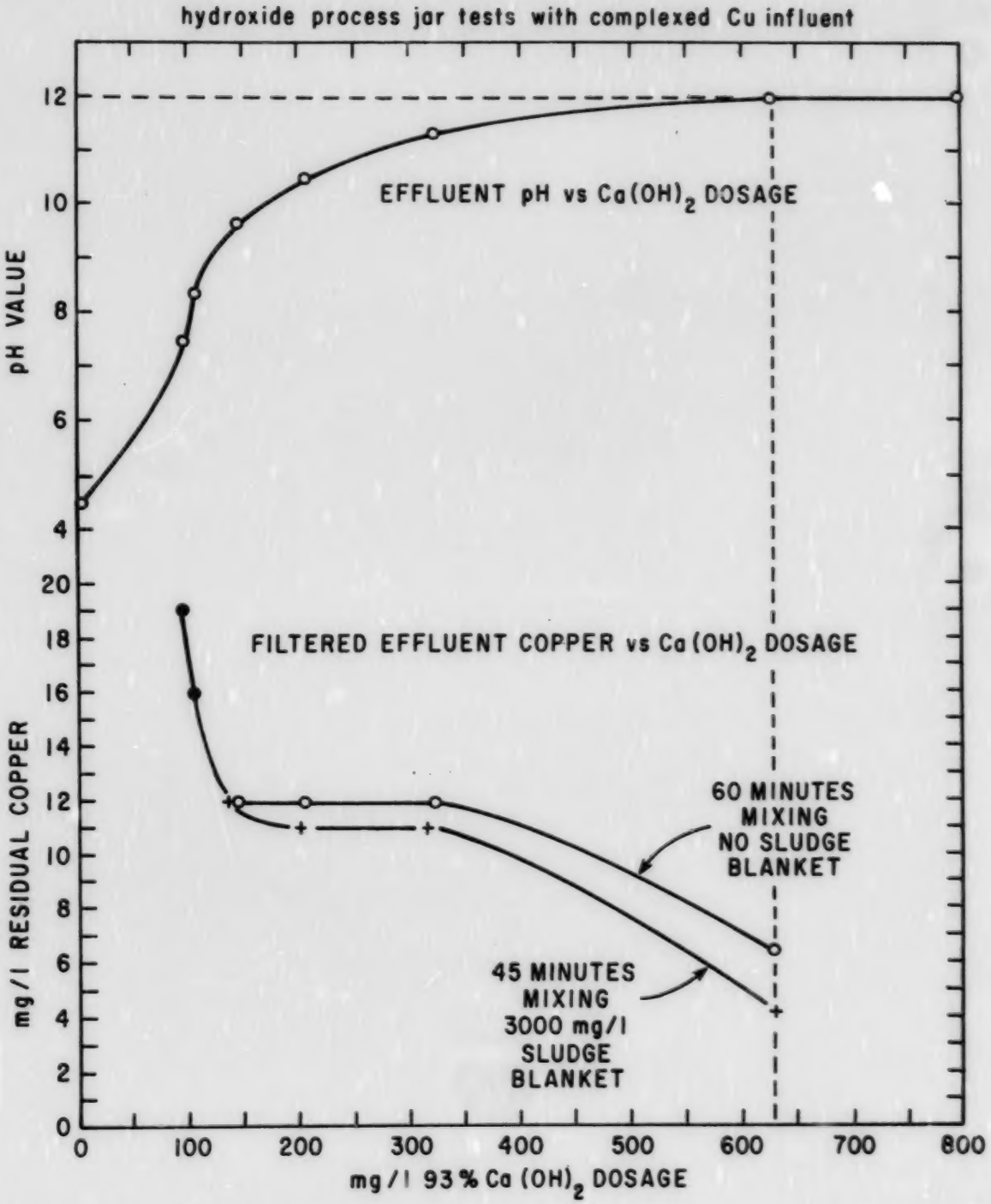


Figure 2. Influence of $Ca(OH)_2$ dosage, sludge blanket concentration and pH valve on copper removal.

Table 4. SULFEX JAR TESTS RESULTS - REMOVAL OF Cu, Cd, Cr (III), Ni, AND Zn WITH AND WITHOUT COMPLEXING AGENTS PRESENT

(X = Theoretical FeS Requirement)
(+ = With Complexing Agents)*
(- = Without Complexing Agents)

		X		1.5X	2X	3X			5X	10X	100X
		Indiv. Ions	Mixed Ions	Mixed Ions	Mixed Ions	Indiv. Ions	Mixed Ions		Mixed Ions	Mixed Ions	Mixed Ions
	pH	-	-	-	-	+	+	-	+	+	+
mg/l Cu	8						0.15	0.02			
	9	0.02	0.01	0.04	0.02		0.19	0.1			
	10					0.18	<.005	0.02	0.07	0.01	0.04
mg/l Cd	8						0.85	0.02			
	9	0.04	0.01	0.02	0.04		0.9	<0.01			
	10					2.9	0.71	<0.01	0.24	0.01	0.01
mg/l Cr	8						2.6	0.29			
	9	<0.05	<0.05	<0.05	<0.05		2.9	<0.1			
	10					0.41	0.41	<0.1	2.9	2.0	1.2

* Complexing agents include 45 mg/l EDTA and 127 mg/l Rochelle salt.

Table 4. SULFEX JAR TESTS RESULTS - REMOVAL OF Cu, Cd, Cr (III), Ni, AND Zn WITH AND WITHOUT COMPLEXING AGENTS PRESENT (CONT.)

(X = Theoretical FeS Requirement)
(+ = With Complexing Agents)*
(- = Without Complexing Agents)

		X		1.5X	2X	3X			5X	10X	100X
		Indiv. Ions	Mixed Ions	Mixed Ions	Mixed Ions	Indiv. Ions	Mixed Ions		Mixed Ions	Mixed Ions	Mixed Ions
	pH	-	-	-	-	+	+	-	+	+	+
mg/l Ni	8						3.6	0.33			
	9	0.64	0.05	0.08	0.02		3.6	<0.05			
	10					2.6	0.71	<0.05	3.4	3.1	2.7
mg/l Zn	8						0.85	0.1			
	9	0.01	0.01	0.06	0.05		0.54	0.01			
	10					1.3	0.21	0.04	0.38	0.22	0.04
mg/l Fe	8						1.5	0.28			
	9	<0.05	<0.05	<0.05	<0.05		0.75	0.05			
	10					<0.05	<0.05	0.05	0.56	0.24	0.2

* Complexing agents include 45 mg/l EDTA and 127 mg/l Rochelle salt.

d. One to one and a half equivalents of sulfide per equivalent of heavy metal is sufficient to reduce the residual concentration of each heavy metal to the desired level when no complexing agents are present. When complexing agents (EDTA and Rochelle salt) are present, higher sulfide dosages are necessary to achieve the desired removal of copper, cadmium, and zinc. Complexed nickel and chrome were not reduced to the desired levels with economically acceptable dosages of sulfide. However, removal of complexed nickel may be improved by operating at pH values greater than pH 10.

Jar tests were also performed to determine the influence of Rochelle salt and EDTA concentrations on the precipitation of copper, cadmium, chromium, copper, and zinc by both sulfide and hydroxide precipitation. In these tests, solutions containing all five metals, each at a concentration of 4 mg/l, were used. To these solutions either Rochelle salt or EDTA was added at its standard concentration (127 mg/l for Rochelle salt, 45 mg/l for Na_4EDTA). Also, to determine the effect of the presence of both Rochelle salt and EDTA, the two complexing agents were combined in the five metal solutions as fractions of their standard concentration. The results of these tests are shown in Table 5. These results indicate that treatment with the Sulfex process reduces all the heavy metal concentrations to substantially lower values than treatment with the hydroxide precipitation process except for Chrome III which is reduced to about the same concentration by both processes. For most heavy metals, the presence of EDTA has a more deleterious effect on the removal of the heavy metals than the presence of Rochelle salt (i.e. tartrate ion). However, the presence of Rochelle salt does interfere with the removal of Chrome III more severely than does EDTA. The results of the jar tests also indicate that Chrome III removal, even in the Sulfex process, is as chrome hydroxide.

Jar tests were also made on an actual metal finishing waste which contained 32 mg/l of total chromium of which 25 mg/l was dissolved hexavalent chromium. This sample also contained 5.9 mg/l of dissolved zinc and traces of copper, iron, and manganese. The presence of strong complexing agents was assumed to be low or absent. Sulfex was tested to determine its effectiveness in removing the hexavalent chromium without the conventional preliminary step of adding a reducing agent at low pH (such as sodium

Table 5. JAR TEST RESULTS SHOWING INFLUENCE OF ROCHELLE SALT AND EDTA CONCENTRATION ON PRECIPITATION OF FIVE HEAVY METALS - COMPARING HYDROXIDE & SULFEX TREATMENT

Each solution contains 4 mg/l of each metal
Hydroxide tests at pH 9.0, Sulfex tests at pH 8.3 - 8.5

Complex Conc.	mg/l Cu		mg/l Cd		mg/l Cr		mg/l Ni		mg/l Zn		mg/l Fe	
	OH	FeS*	OH	FeS*	OH	FeS*	OH	FeS*	OH	FeS*	OH**	FeS*
A												
Std. Complex Conc. 127 mg/l Rochelle 45 mg/l EDTA	1.2	0.01	4.4	2.9	0.47	0.40	1.8	0.88	1.5	1.4	--	0.31
B												
Std. Rochelle Conc. only 127 mg/l Rochelle	0.18	<0.01	0.67	<0.01	0.20	0.20	1.2	0.18	0.02	0.02	--	0.20
C												
Std. EDTA Conc. only 45 mg/l EDTA	1.8	<0.01	4.8	2.9	<0.05	<0.05	1.3	1.4	2.2	1.5	--	0.12

* FeS represents Sulfex treatment

** No Fe was added to system in the hydroxide precipitation tests.

Table 5. JAR TEST RESULTS SHOWING INFLUENCE OF ROCHELLE SALT AND EDTA CONCENTRATION ON PRECIPITATION OF FIVE HEAVY METALS - COMPARING HYDROXIDE & SULFEX TREATMENT (cont.)

Each solution contains 4 mg/l of each metal
Hydroxide tests at pH 9.0, Sulfex tests at pH 8.3 - 8.5

Complex Conc.	mg/l Cu		mg/l Cd		mg/l Cr		mg/l Ni		mg/l Zn		mg/l Fe	
	OH	FeS*	OH	FeS*	OH	FeS*	OH	FeS*	OH	FeS*	OH**	FeS*
D												
½ Complex Conc. of A	0.25	0.01	3.2	2.0	0.12	0.05	1.2	0.49	0.15	0.63	--	0.08
E												
¼ Complex Conc. of A	0.14	<0.01	2.4	1.3	<0.05	<0.05	1.1	0.33	0.05	0.27	--	<0.05
F												
1/10 Complex Conc. of A	0.04	<0.01	1.3	0.42	<0.05	<0.05	1.0	0.18	0.02	0.06	--	<0.05

* FeS represents Sulfex treatment

** No Fe was added to system in the hydroxide precipitation tests.

metabisulfite) to convert the hexavalent chrome to trivalent chrome[5]. The results of these tests show that between 50 and 100 mg/l of ferrous sulfide (about the same dosage as that required for removal of 20 mg/l of complex copper) is sufficient to reduce the effluent total chrome level to less than 0.05 mg/l (as Cr) and the effluent zinc level to about 0.05 mg/l (as Zn). Therefore, a one step Sulfex process appears to be a very effective method of removing hexavalent chrome as well as other heavy metals from solution.

REFERENCES

5. Ward, A. E. Chapter 11, Wastewater Control and Treatment. In: Electroplating Engineering Handbook, 3rd ed., Graham, A. K. (ed.), New York, New York, Van Nostrand Reinhold Company, 1971, pp. 359-360.

SECTION V

PILOT PLANT STUDIES

A. Description of Pilot Plant

The Sulfex pilot plant was assembled and piped in The Permutit Research and Development Center which is located in Princeton, New Jersey. A flow plan of the pilot plant is shown in Figure 3. Figure 4 shows cross-sectional views of the Precipitator used in the pilot plant system.

Supply to the Precipitator was a mixture of well water and a prepared solution containing the desired metals. Well water was pumped through a 2 inch inlet line to the upper part of the mixing zone of the Precipitator. The complexed copper plating solution and additional metals were fed into the inlet line, by means of chemical metering pumps, approximately 25 feet upstream of the Precipitator. The flow rates of the well water and metal solutions were controlled to provide the desired metal concentrations in the influent to the Precipitator.

Preparation and feed of treatment chemicals was accomplished in the following manner. Freshly precipitated ferrous sulfide (FeS) slurry was introduced into the influent line just prior to entering the Precipitator mixing zone. The ferrous sulfide slurry was produced by reacting sodium hydrosulfide and ferrous sulfate in a 10 gallon head tank under rapid stirring. A 1.5 gpm dilution water stream entered the bottom of the slurry tank where it was detained and mixed for about 7 minutes. Sodium hydrosulfide (as a 45% solution of NaHS) was fed, by means of a small chemical metering pump, to the dilution water line before entering the head tank. Ferrous sulfate ($FeSO_4$) solution and lime ($Ca(OH)_2$) slurry were metered into the sodium hydrosulfide solution in the FeS head tank.

The influent, dosed with fresh FeS slurry, passed downward through the mixing zone where it was mixed with accumulated, previously precipitated FeS particles. At the bottom of the mixing zone, the stream changed direction and flowed upward through the port area into the settling zone. The cross-sectional area perpendicular to the upward flow continuously increased so that the upward flow velocity continuously decreased and allowed the precipitated solids to settle out of the upward moving liquid. At the top of the settling zone, the liquid surface was covered with chevron settlers which settled out most of the fine or light precipitates that did not

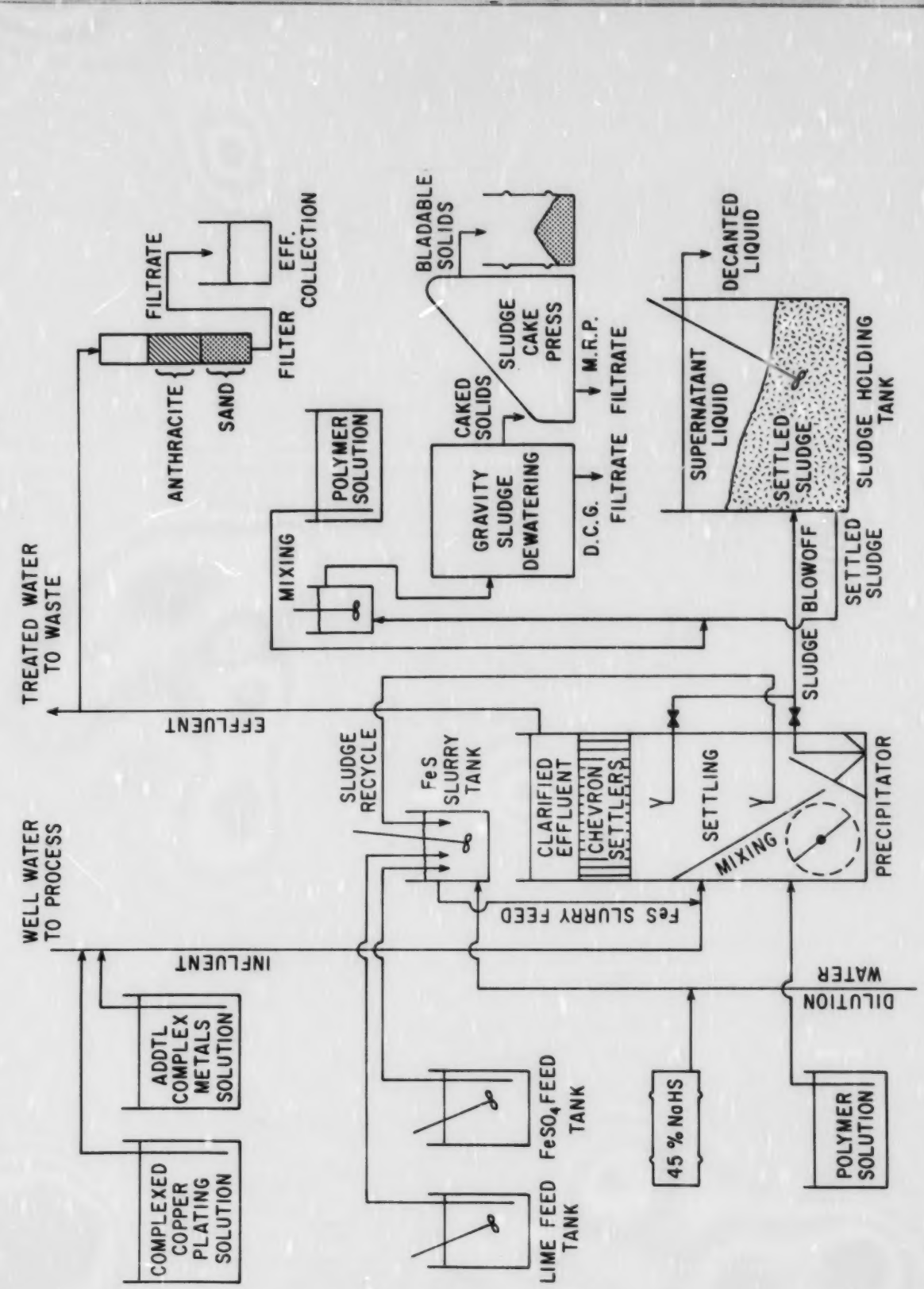


Figure 3. Sulfex pilot plant flow plan.

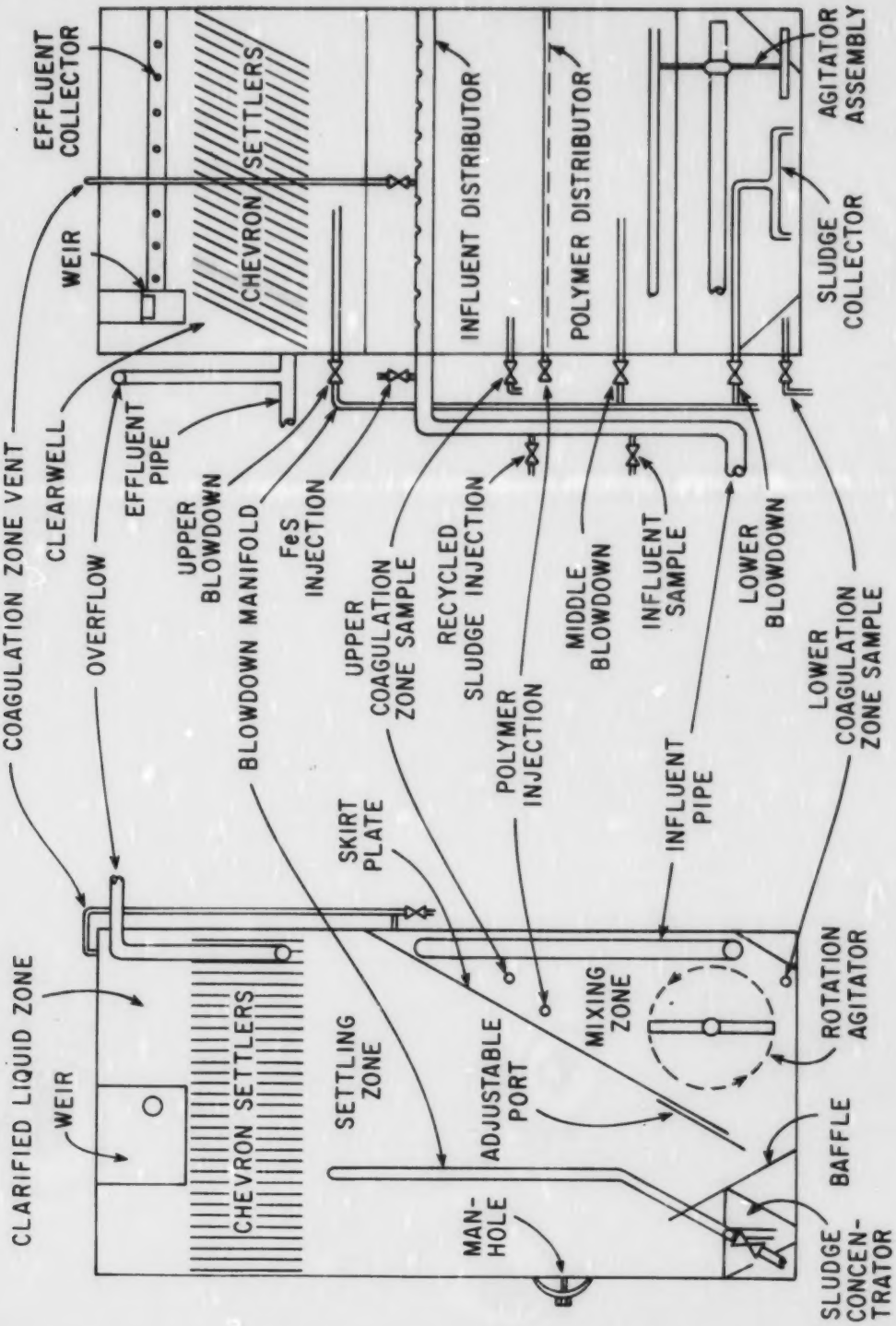


Figure 4. 5'-8" wide x 5'-6" long x 11'-0" high package Precipitator with chevron settlers.

settle in the lower part of the settling zone. A very concentrated fluidized sludge blanket accumulated in the settling zone to achieve additional solids-liquid contact time. The clarified liquid then rose out of the chevron settlers establishing a clear liquid zone at the top of the Precipitator.

The clarified liquid flowed, by gravity, through an effluent collection pipe into the effluent line. For these tests, most of the Precipitator effluent was discharged directly to waste. A small portion (0.5 gpm) of the Precipitator effluent was introduced into a 4.75 inch I.D. filter column containing 12 inches of fine sand as a bottom media layer and 18 inches of fine anthracite as a top media layer. The effluent from the filter was collected in a tank to obtain composite effluent samples.

Both the sludge accumulated in the concentrator at the bottom of the Precipitator, and the sludge accumulated in the top of the sludge blanket (just below the bottom of the chevron settlers) was discharged periodically through blowoff lines into a sludge holding tank; therefore, it was not necessary to continuously operate the dewatering equipment.

When sufficient sludge was accumulated in the sludge holding tank, the sludge was pumped via a diaphragm sludge pump to a head tank ahead of the DCG (Dual Cell Gravity) filter. Here, a polyelectrolyte solution was metered into and mixed with the sludge before entering the DCG so that the sludge was conditioned into large firm particles. After this conditioning stage, the sludge was gravity fed to the DCG where it was changed from a fluidized sludge to a moist cake by a gravity dewatering method. In this unit, the loose liquid was separated from the solids by a moving screen. The loose liquid, called the filtrate, was discharged to waste. The solids collected on the screen, called the cake, was discharged to the MRP unit.

The MRP or Multi Roller Press enabled further dewatering of the DCG cake discharge. This unit pressed more water out of the sludge cake and changed it from a moist cake-like solid to a dryer bladeable solid. The liquid forced out of the sludge cake by the MRP was drained, by gravity, out of the bottom of the unit to waste. The pressed solid then dropped from the end of the MRP into a 50 gallon drum in which it was collected for disposal.

Provisions were made for a portion of the sludge blanket, in the lower settling zone of the Precipitator, to be recycled back into the FeS head tank in order to increase the concentration of solids in the FeS feed. If desired, sludge could also be recycled from the concentrator at the bottom of the Precipitator or from the mixing zone. However, the lower settling zone was used since this sludge was fresher than either the sludge in the upper settling zone or that in the concentrator. Although the sludge in the mixing zone was fresher than that in the lower settling zone, the sludge concentration was much higher in the lower settling zone. The lower settling zone, therefore, appeared to be the best point source of a high concentration of relatively fresh sludge.

This pilot plant was also used for the Precipitator tests of the hydroxide process. For these tests, no ferrous sulfate or sodium hydrosulfide were fed and the lime, as $Ca(OH)_2$, was introduced directly into the inlet line instead of into the head tank (FeS slurry tank). All other details shown in Figure 3 remained the same.

B. Sulfex Precipitator Tests with 20 mg/l Complexed Cu in Influent

The objective of the initial Precipitator tests was to optimize those parameters which were found to be important in the jar tests. Since the jar tests in which the effects of operating parameters were studied used the complexed copper waste, these Precipitator tests were also performed using the complexed copper waste (see Table 3, Column II). Other Precipitator tests were then performed to study the effect of variable influent compositions on operating results.

1. Parameters Studied in the Precipitator Tests

The parameters which were found to be important for copper removal in the jar tests were tested in the Precipitator. These were: (1) ferrous sulfide dosage, (2) ferrous sulfide sludge blanket solids concentration, (3) ferrous sulfide sludge blanket mixing time with the liquid waste, and (4) use of a cationic polyelectrolyte to aid sedimentation of precipitated solids. Other parameters which were also studied included (5) agitator mixing speed, (6) effluent pH, (7) sludge recycle, (8) high iron concentrations in the complexed copper influent, (9) different concentrations of copper in the influent, and (10) the inclusion of five heavy metals in the influent.

a. Ferrous Sulfide Dosage

The dose of freshly precipitated ferrous sulfide introduced into the influent has a significant effect on the level of residual copper in the effluent. The Precipitator was operated using 2 to 4 times the number of equivalents of ferrous sulfide which are theoretically needed to precipitate 20 mg/l of copper. The Precipitator tests show, for the simulated waste containing 20 mg/l of copper complexed with Rochelle salt and EDTA, that the optimum dosage is about three times the theoretical (stoichiometric) requirement.

Initially, the Precipitator was operated at FeS dosages of 2 times theoretical and 4 times theoretical. The pH range for these initial tests was maintained between 7.0 and 8.0. In this pH range, a ferrous sulfide dose of 2 times theoretical (55 mg/l as FeS) is not sufficient to continuously reduce the copper conconcentration to the level which had been set as a goal ($\leq$0.1 mg/l as Cu). In the same pH range (7.0-8.0), but using an increased ferrous sulfide dose of 4 times theoretical (110 mg/l as FeS), the effluent copper is about 0.25 mg/l as Cu (~7.0), 0.15 mg/l as Cu (pH ~7.5), and 0.03 mg/l as Cu (pH ~8.0). A ferrous sulfide dose of 3 times theoretical was not tested in the pH range 7.0 to 8.0 because, as shown above, the results with a ferrous sulfide dose of 4 times theoretical were only acceptable at the upper boundary of this pH range. However, 3 times the theoretical ferrous sulfide dosage was extensively studied in the pH range 8.5 to 9.0. For these conditions, the average effluent copper level is consistently less than 0.1 mg/l as Cu.

Table 6 shows the effects of the different influent rates, ferrous sulfide dosages, effluent pH, and solids concentrations, on both effluent copper and effluent iron concentration. It can be seen that at a given set of conditions, increasing the pH not only reduces the residual copper concentration but also the residual iron concentration. Although iron is only present in the Precipitator influent at about 0.1 mg/l, a significant concentration of iron (as FeS) is introduced into the treatment process. The ability of the Sulfex process to reduce not only the heavy metal concentration but also the iron concentration is significant since no additional equipment is needed for iron removal.

b. Sludge Blanket Solids Concentration

The sludge blanket concentration is defined as the volume of settled solids in a sample of the sludge blanket that has been allowed to settle undisturbed for 10 minutes. This concentration is designated as volume percent solids and represents the percent of the original sample volume that is occupied by the settled portion after 10 minutes of settling.

The results obtained in the jar tests show lower effluent copper concentrations occur when the concentration of sludge blanket solids is increased. The influence of sludge blanket concentration on copper removal was carefully observed in the Precipitator tests. The trends observed in the jar tests are also seen in the Precipitator tests. Increased copper removal coincides with an increased concentration of settleable solids in the mixing zone.

The volume percent solids of both the settling zone and mixing zone of the Precipitator were routinely measured. The data shows the volume percent solids in the mixing zone is more critical than in the settling zone. The critical level of mixing zone solids concentration is about 15 volume percent. If the mixing zone solids concentration is less than 15 volume percent, the effluent copper concentration is usually higher than 0.1 mg/l as Cu. Values above 15 volume percent give copper residuals which are lower than 0.1 mg/l as Cu. The sludge blanket solids concentration in the mixing zone is generally higher than 15 volume percent for influent rates of 20 gpm and 30 gpm. However, at an influent rate of 40 gpm, the mixing zone solids concentration drops below 15 volume percent when a higher rotational speed of the agitator is not maintained.

Table 6 shows the increased effluent copper concentrations that result at 40 gpm as the mixing zone solids concentration decreases while the FeS dose and pH remain constant. Figure 5 also shows the relationship between residual copper concentration and mixing zone volume percent solids. This figure was developed by averaging many data points collected during the Precipitator tests at 30 and 40 gpm flow rates and constant pH.

Table 6. PILOT PLANT EFFLUENT RESIDUALS OF TOTAL COPPER AND IRON AT DIFFERENT LEVELS OF OPERATING PARAMETERS FOR COMPLEXED Cu INFLUENT

Influent Rate (gpm)	FeS Dosage*	Effluent pH Value	Avg. Mixing Zone Solids (vol. %)	milligrams per liter Effluent Quality Avg. Cu	Avg. Fe
20	2X	7.4	35	2.9	10
20	2X	7.6	35	2.9	5.0
20	2X	8.0	35	2.0	2.4
20	2X	9.0	35	0.25	<0.1
20	4X	6.7	45	0.25	25
20	4X	7.4	45	0.15	10
20	4X	8.0	45	0.03	1.0
20	4X	8.7	45	0.01	0.4
30	2X	8.6	22	0.71	<0.1
30	2X	8.7	22	0.70	<0.1
30	2X	8.8	22	0.62	<0.1
30	3X	8.6	26	0.07	0.1
30	3X	8.8	26	0.05	0.1
30	3X	8.9	26	0.03	0.2
40	3X	8.7	18	0.19	0.1
40	3X	8.8	18	0.09	0.3
40	3X	8.9	18	0.05	0.1
40	3X	8.8	8	0.40	0.1
40	3X	8.9	6	0.40	0.1
40	3X	8.9	13	0.21	<0.1
40	3X	9.0	11	0.25	<0.1

* X = Theoretical concentration required to react with 20 mg/l Cu^{++}

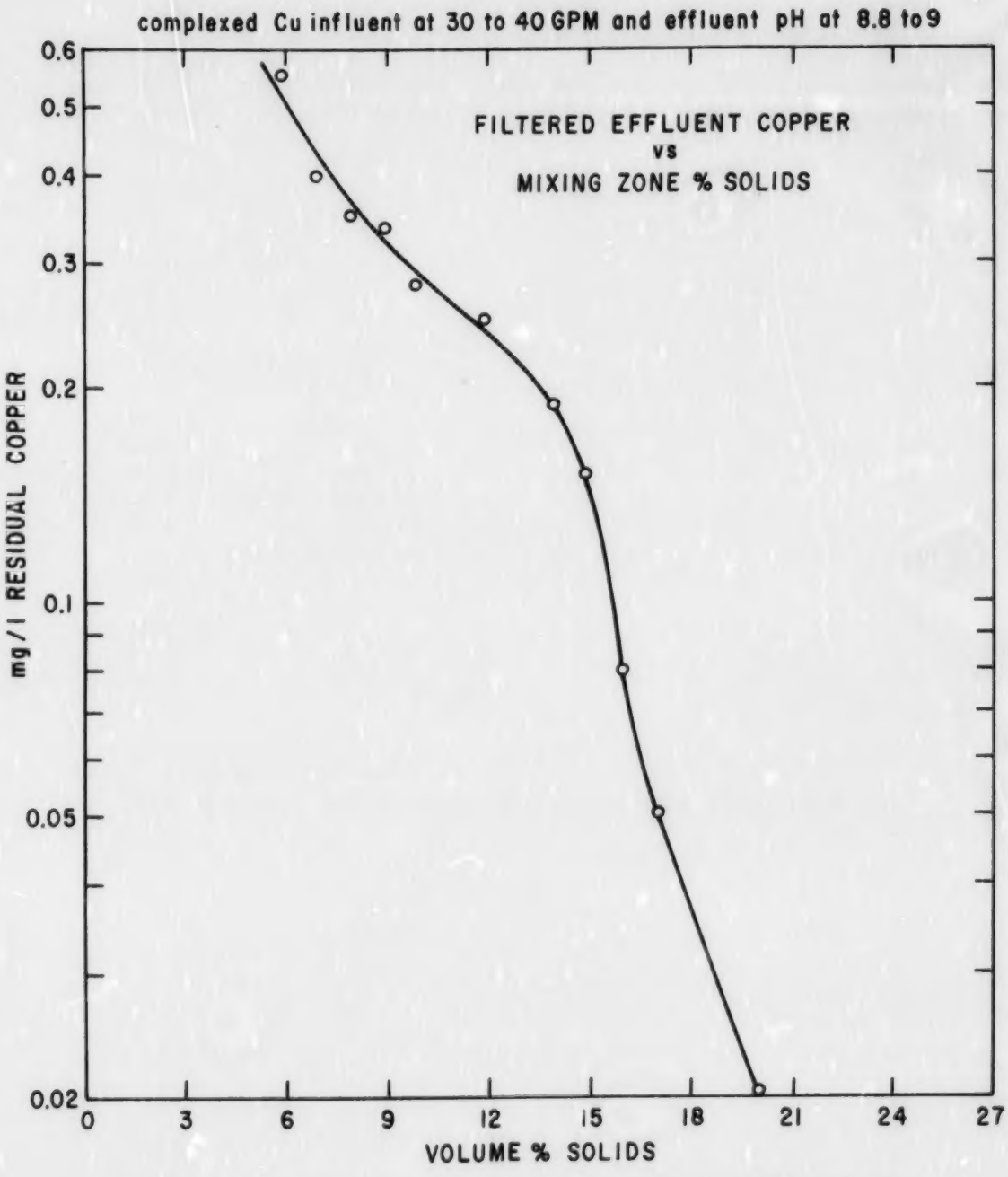


Figure 5. Influence of mixing zone solids concentration on copper conentration of filtered effluent.

c. Sludge Blanket Contact Time with Liquid Waste

Changing the influent flow rate to the Precipitator changes the detention time in both the mixing zone and settling zone and, therefore, the length of sludge blanket contact time with the liquid waste. At 20 gpm (1.0 gpm/ft^2 surface rate), the detention time in the mixing zone is about 25 minutes followed by 75 minutes detention in the settling zone. At 30 gpm (1.5 gpm/ft^2 surface rate), the mixing zone contact time is about 17 minutes followed by 51 minutes of detention in the settling zone. At 40 gpm (2.0 gpm/ft^2 surface rate), the mixing zone contact time is about 12.5 minutes followed by 37.5 minutes of detention in the settling zone. An effluent containing 0.1 mg/l or less copper is produced, provided the other operating parameters are maintained at their optimum conditions, at all three flow rates. This shows a total contact time of approximately one hour is sufficient to achieve the desired results.

In addition to studying the copper removal as a function of the total sludge blanket contact time, copper removal at different stages (contact times) in the Precipitator was determined. The results of these tests are shown in Table 7. This data shows that 95 to 98 percent of the complexed copper is removed during the first 10 minutes of contact (i.e. mixing zone). During the remainder of the contact time in the Precipitator, less than 1 mg/l of copper is removed. However, this last period of extended sludge blanket contact is important because it reduces the quantity of suspended and colloidal metal sulfides that will be carried over in the effluent.

d. Use of a Coagulant Aid

The cationic guar gum derivative polyelectrolyte which was found most effective in the jar tests was successfully used in the Precipitator tests. The polymer was fed (as a 0.05 to 0.1 weight percent solution) directly into the lower part of the mixing zone with a metering pump. A distributor tube running across the Precipitator uniformly distributed the polymer solution in the mixing zone. The supernatant was very turbid when no coagulant aid was used during the jar tests. Therefore, no Precipitator tests were made without the polyelectrolyte.

Table 7. COPPER REMOVAL IN VARIOUS STAGES OF THE PRECIPITATOR FOR COMPLEXED Cu INFLUENT

(Stage 1 to 4 Cu concentrations are for 0.45 micron filtered samples)

Stage	Run	A	B	C	D	E
	FeS Dose	2X	4X	4X	4X	2.4X
	Effluent pH	7.4	7.0	7.3	6.8	8.9
1	Influent Cu^{++} (contact time = 0 min)	18	18	20	20	23
2	Upper Mixing Zone Cu^{++} mg/l (contact time = 5-10 min)	3.2	0.9	0.89	0.76	0.45
3	Lower Settling Zone Cu^{++} mg/l (contact time = 30 min)	2.8	0.3	0.54	0.44	0.10
4	Precipitator Effluent Cu^{++} mg/l (contact time = 100 min)	2.9	0.2	0.41	0.31	0.10
5	Sand Filter Effluent (total contact time = 115 min)	2.9	0.2	0.41	0.22	0.05

The Precipitator was started at 20 gpm using 3 mg/l of polymer to build the sludge blanket. Once the sludge blanket is formed, the effluent turbidity is low (generally less than 1 JTU). When the polymer dose is reduced to 1.5 mg/l, the turbidity remains less than 1 JTU, but the settleable solids concentration in the mixing zone decreases significantly. When the polyelectrolyte concentration is subsequently increased to 4 mg/l, at influent flow rates of both 20 gpm and 30 gpm, very clear Precipitator effluents are obtained. Under these conditions, it is possible to operate the sand filter for periods of 40 hours or more before backwashing is needed. When the influent flow rate is increased to 40 gpm, the polyelectrolyte dose has to be increased to 5 or 6 mg/l in order to maintain low effluent turbidities (less than 1 JTU) and a sufficient mixing zone solids concentration (greater than 15 volume percent).

e. Agitator Mixing Speed

The speed of the agitator in the mixing zone of the Precipitator is not critical at the 20 to 30 gpm flow rates, but it is important at the 40 gpm flow rate. The tip speed of the agitator used is 0.13 ft/sec. per rpm. Initially, when the Precipitator was operating at 20 gpm, more rapid sludge blanket formation occurred at agitator speeds of 10 to 12 rpm than at 5 rpm. Then, increasing the agitator speed from 12 rpm to 14 rpm increased the average mixing zone solids concentration from about 35 volume percent to about 45 volume percent. This was beneficial. However, further increases in agitator speed from 14 rpm to 22 rpm resulted in only a temporary increase in the mixing zone solids. Over an 8 hour period it returned to 45 volume percent solids.

Agitator speeds of 11 to 14 rpm at 20 and 30 gpm flows are sufficient to maintain a mixing zone solids concentration above 15 volume percent solids, once the sludge blanket is formed. Lowering the agitator speed (i.e. to 7 rpm) at either 20 gpm or 30 gpm has no immediate or significant influence on the mixing zone solids concentration. Therefore, the agitator speed does not appear to be a critical influence on effluent quality at flow rates below 30 gpm. When testing agitator speeds at Precipitator flow rates which are greater than 30 gpm, it is found that the speed of the agitator has more influence on the mixing zone solids concentration and, hence, on the effluent quality. At the 40 gpm flow rate (the highest flow rate tested), it is found that the speed of

the agitator had to be kept sufficiently high in order to maintain the mixing zone settleable solids concentration above the critical value of 15 volume percent. For example, lowering the agitator speed from 11 rpm to 7 rpm allows the mixing zone solids concentration to gradually decrease from about 20 volume percent to about 6 volume percent. When the agitator speed is then increased back to 11 rpm, the mixing zone solids concentration increases to 20 volume percent where it levels out. This increase of agitator speed, therefore, accelerates growth of metal sulfide precipitates into settleable sized particles.

For this pilot plant Precipitator, the 11 rpm agitator speed maintains an average solids concentration of about 20 volume percent at 40 gpm, 25 volume percent at 30 gpm, and 40 volume percent at 20 gpm. Although the required agitator speed at any flow rate will vary with the design of the Precipitator, it has to be fast enough to bring about rapid agglomeration of the precipitates without causing shearing of settleable sized particles into smaller particles that will be swept out of the Precipitator by the flowing liquid.

f. Effluent pH Value

As already indicated in the discussion of FeS dosage, the pH of the reaction has a significant effect on the effluent quality. The pH of the Precipitator effluent is essentially the same as the pH in the mixing and settling zones. However, it is more stable and, therefore, is used in this study to represent the equilibrium pH of the system.

When operating the Precipitator in the pH range of 7.0 to 8.0, there is no clearcut relationship between complexed copper removal and effluent pH. However, the removal of iron improves with increasing pH in this range. When the pH is increased to values of 8.5 or greater, the importance of pH on effluent quality becomes very apparent. Figure 6 shows that operating the process in the 8.5 to 9.0 pH range gives significantly lower copper and iron residuals in the effluent than operating in the 7.0 to 8.0 pH range, all other conditions remaining equal. Since both complexed copper and iron are reduced to very low residuals in the pH range of 8.5 to 9.0, this range is established as the optimum range for the given influent.

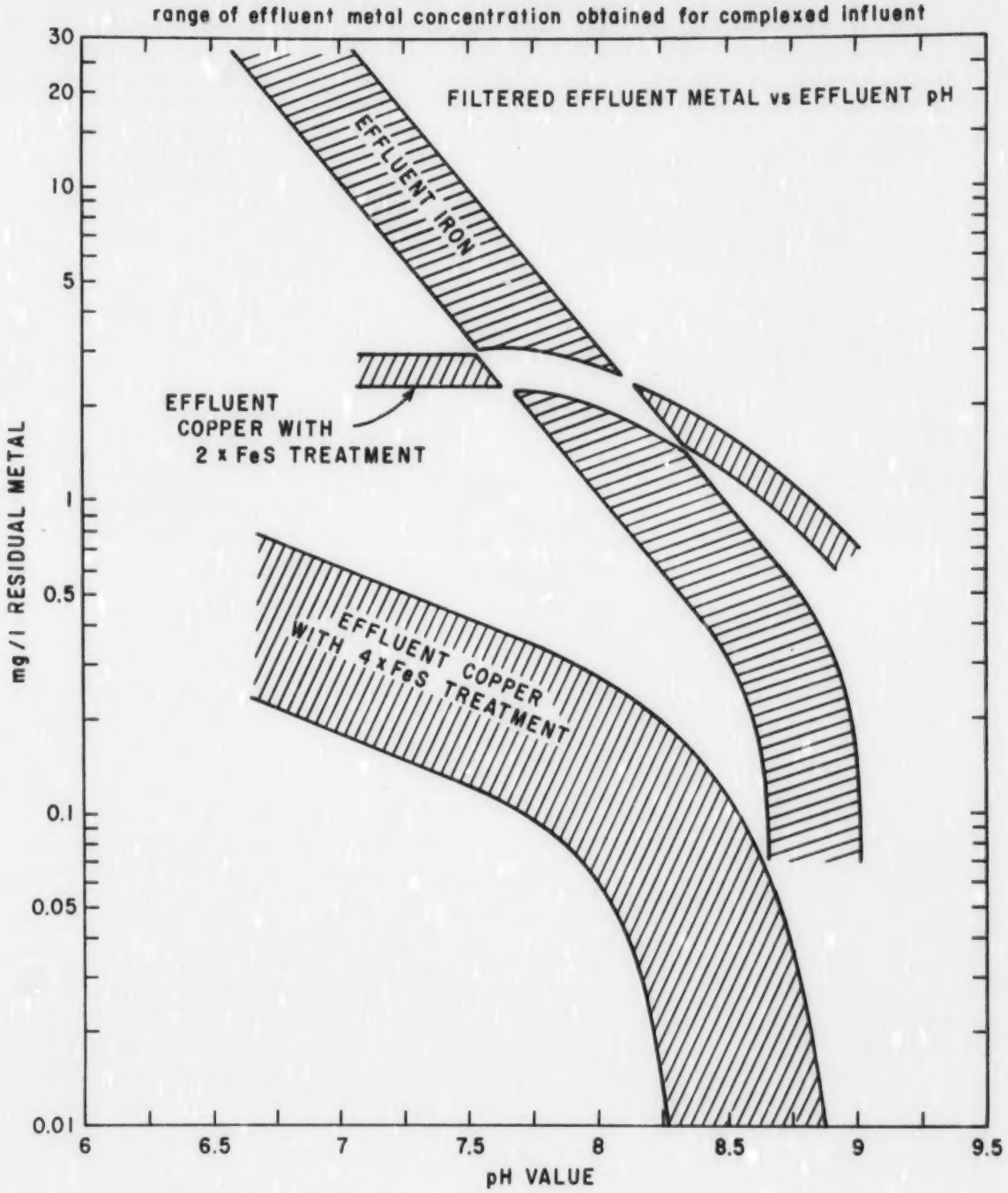


Figure 6. Relationship of effluent pH value to filtered effluent copper and iron concentrations.

g. Sludge Recycle

One way of improving the effluent quality without increasing the FeS dosage was expected to be by recycling the sludge from either the settling zone or concentrator back to the influent line. To make more FeS available during the mixing stage of the process, it was proposed that the partially reactive sludge from the settling zone and/or concentrator could be re-exposed to the influent stream. It also was thought the recycled sludge would increase the settleable solids concentration in the mixing zone which has already been discussed as being beneficial to copper removal.

Sludge recycle was tested at 20, 30, and 40 gpm influent rates. The volume of sludge recycled was approximately 1 gpm, and it was pumped from the lower settling zone into either the influent line directly or into the FeS slurry tank. The lower settling zone was selected as the source of the sludge recycle because it contained a lower percent of precipitated copper than the other zones of high sludge accumulation. Thus, it is apparently the fresher source of sludge. Table 8 shows the relative percentages of copper and iron in the sludges found in the settling zones and concentrator.

With the sludge recirculation, the volume percent of sulfide solids introduced into the Precipitator influent was increased by 50 to 125 percent over the amount added by the fresh FeS. The sludge recycled to the influent is not the same as increasing the fresh FeS slurry by 50 to 125 percent, since the recycled sludge contains unreactive solids such as copper sulfide and iron hydroxide.

At an influent rate of 40 gpm, there were periods when the sludge recycle appeared to give lower effluent copper values. However, most of the time the use of sludge recycle did not improve the effluent quality at any of the flow rates tested when all other operating conditions were maintained at optimum levels. Since good results are obtained without sludge recycle, it is not used in the Precipitator tests using the other influent compositions.

Table 8. SLUDGE COMPOSITION FROM VARIOUS PRECIPITATOR ZONES

	Upper Settling Zone	Lower Settling Zone	Concentrator
Copper % (wt/wt)	6.0	3.2	4.5
Iron % (wt/wt)	30	14	24
Suspended Solids (mg/l)	3000	6500	11,500

2. Sulfex Precipitator Optimization Test

After the optimum level of each operating parameter was determined in the Precipitator for treating a 20 mg/l complexed copper feed, a continuous 10-day test run was made. The optimum levels were maintained during this test run. These levels were:

a. The Precipitator was operated at 30 gpm. This flow rate represented a moderate surface rate (1.5 gpm/ft^2) through the Precipitator.

b. The FeS dosage (85 mg/l as FeS) was maintained at 3 times the stoichiometric requirement.

c. The pH value in the Precipitator was controlled between 8.5 and 9.0.

d. The mixing zone settleable solids concentration was maintained above 15 volume percent.

e. The cationic polyelectrolyte concentration was maintained at 4 to 6 mg/l in the mixing zone.

Figures 7 and 8 show the conditions and results, respectively, of the operating parameter study and optimization test. In these figures, the levels of copper and iron in the Precipitator influent and in the filter effluent (Figure 8) and other pertinent operating parameters (Figure 7) are plotted versus the operating time. The results show that when the operating parameters are maintained at the optimum levels, the effluent copper concentration is maintained below 0.1 mg/l total copper. During the optimization test, the effluent quality under optimum conditions never increased above 0.1 mg/l total copper. The two occurrences of Cu levels greater than 0.1 mg/l were caused by a failure of the NaHS feed and a breakthrough of the filter. Therefore, these points should not be included in the evaluation. However, it should be noted that the filtered effluent quality dropped below 0.1 mg/l total copper again after the filter was backwashed. In Figures 7 and 8, the operating period between 415 hours and 475 hours represents the optimization test.

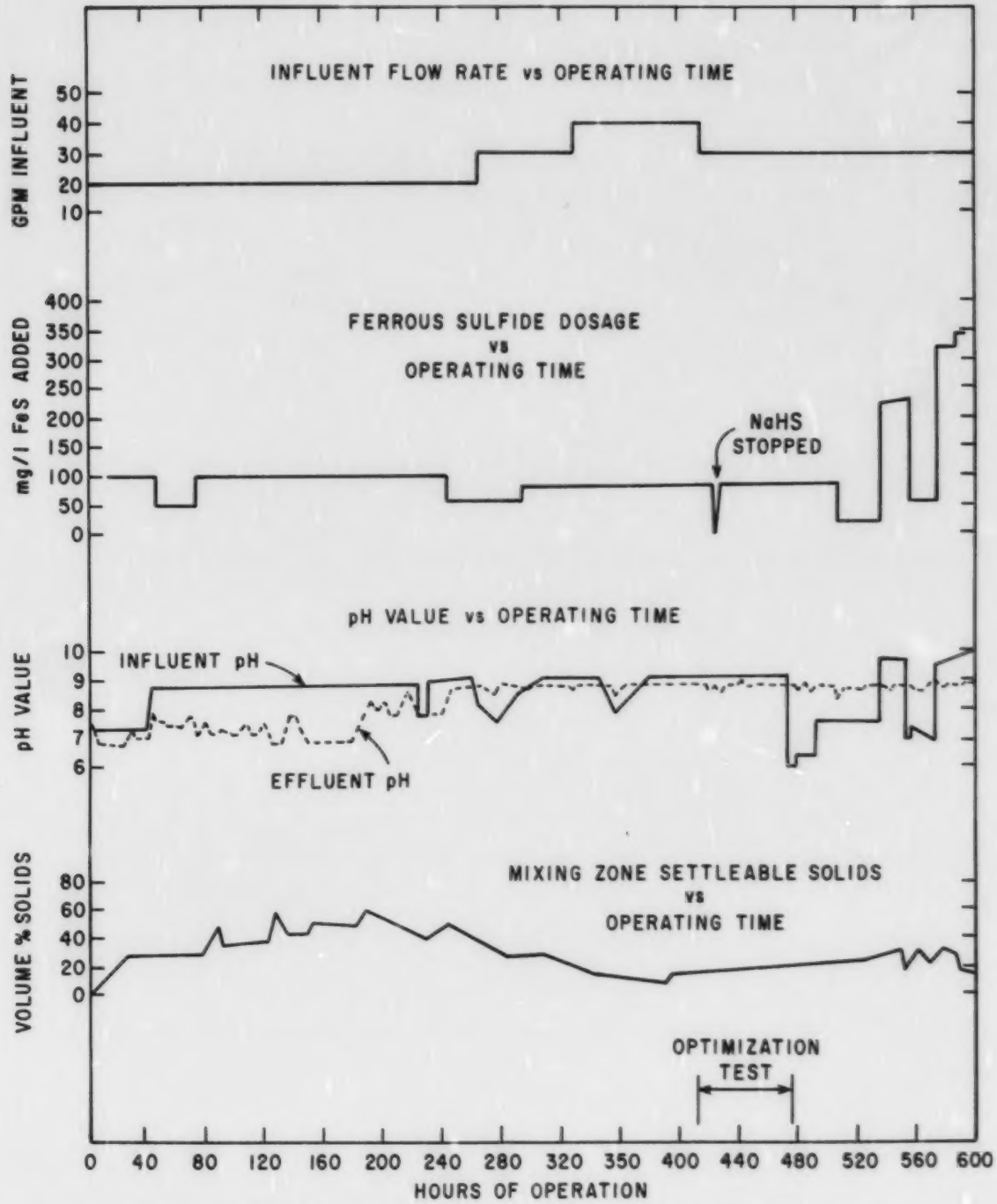


Figure 7. Precipitator operating data for removal of complexed copper.

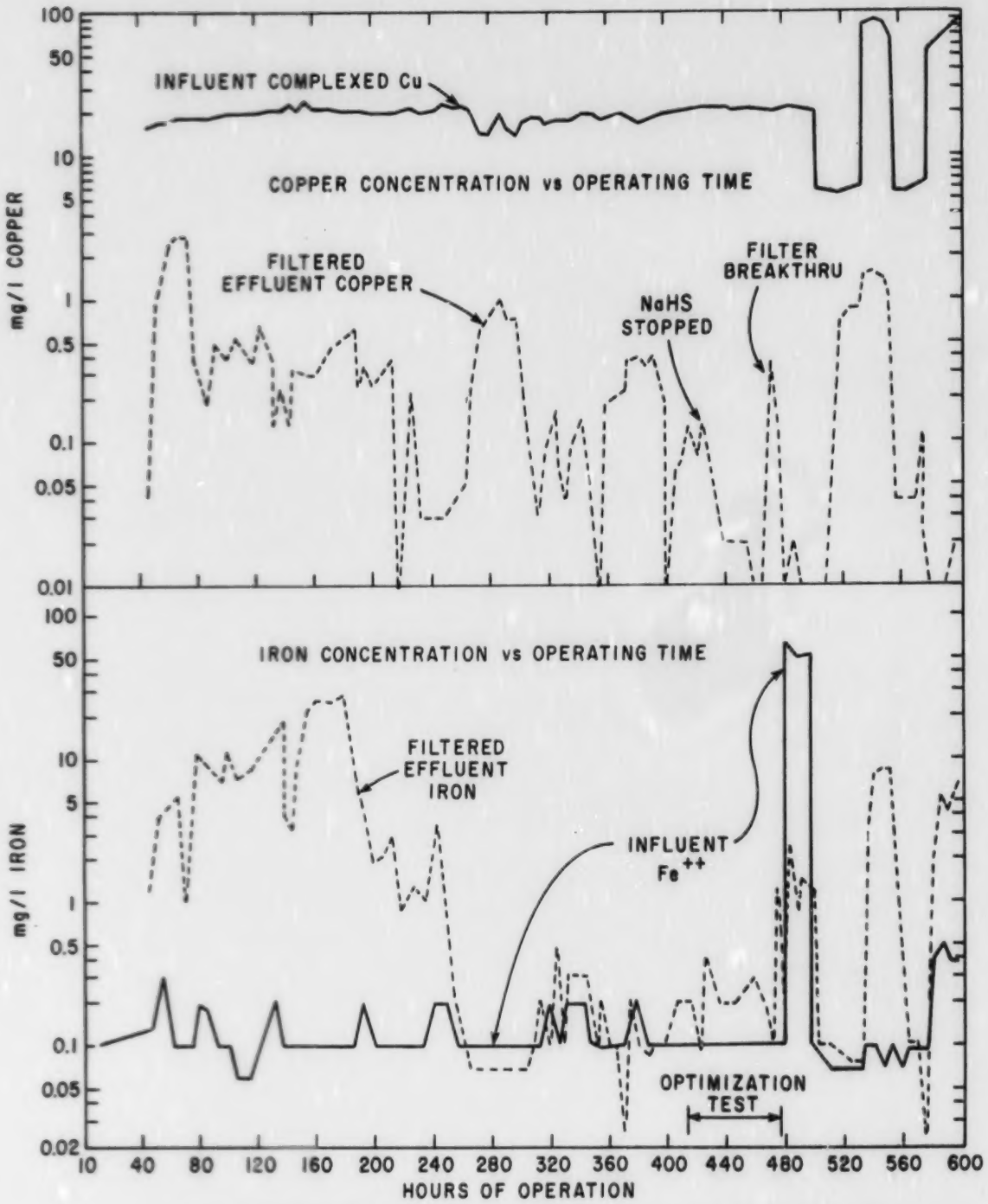


Figure 8. Precipitater operating results for removal of complexed copper.

3. Conclusions of Sulfex Tests with 20 mg/l Copper Complexed with Rochelle Salt and EDTA

The 5.5 ft. long x 5.7 ft. wide x 11 ft. high Permutit Package Precipitator followed by a filter can be successfully used for removal of complexed copper ions from an influent stream at flow rates up to 40 gpm. The following optimum conditions have to be maintained for successful operation.

a. FeS dosage at least 2.5 to 3 times stoichiometric.

b. Mixing zone settleable solids concentration equal to or greater than 15 volume percent.

c. Mixing zone cationic polyelectrolyte concentration equal to 4 to 6 mg/l.

The Precipitator effluent can be successfully polished with a dual media sand and anthracite filter to contain less than 0.1 mg/l total copper at the optimum operating conditions. Recycling of the sulfide sludge from the sludge blanket to the Precipitator influent does not significantly improve the effluent quality when the operating conditions are maintained at optimum levels.

4. Study of Optimized Sulfex Process on Influent Containing 20 mg/l Copper and 50 mg/l Ferrous Iron Complexed with Rochelle Salt and EDTA

a. Precipitator Tests

Figures 7 and 8 include the results of the test with high dissolved iron concentrations in the influent in addition to the complexed copper (i.e. influent shown in Column II, Table 3 + 50 mg/l Fe^{++}). The operating period between 476 hours and 496 hours represents this test. During this period, the influent copper averaged 21 mg/l as Cu, and the influent dissolved iron averaged more than 50 mg/l as Fe. The operating parameters were maintained at optimum levels with about 3 times theoretical FeS dosage (75 to 80 mg/l as FeS), 20 to 22 volume percent solids in the mixing zone, and an effluent pH in the range 8.6 to 9.0. Due to the increased amount of iron added to the influent, the influent pH was lower (6.1 to 7.6) than for the influent composition shown in Column II, Table 3 (pH 8.8 to 9.0). The effluent pH was raised to the optimum level (8.5 to 9.0) by increasing the lime dosage to the FeS slurry tank. The influent flow rate to the Precipitator was maintained at 30 gpm during this test.

The goal of an effluent Cu concentration of equal to or less than 0.1 mg/l was adhered to during this test. However, the effluent iron level (about 1.5 mg/l) had increased to levels higher than those resulting from tests with much lower influent dissolved iron levels ($\leq$0.2 mg/l as Fe).

b. Conclusions

The conclusions made from the Precipitator test, with an influent containing both complexed copper and a high concentration of complexed iron, is that the influent iron concentration has no deleterious influence on the removal of the copper. However, the presence of the complexing agents with the high influent dissolved iron does tend to give higher than expected effluent iron concentrations. In the cases where high dissolved iron concentrations together with the presence of strong complexing agents is a problem, there are two possibilities for obtaining lower effluent iron concentration.

(1) Increase the pH in the Precipitator (i.e. to 10-10.5) so that the hydroxide of ferrous iron becomes less soluble in the system.

(2) Add an oxidizing agent to the filter effluent to oxidize the ferrous iron to ferric iron since ferric hydroxide is less soluble at pH 8.5 to 9.0 than ferrous hydroxide. Then, pass the effluent through a second filtering step to remove the precipitated iron.

C. Sulfex Tests with 5 mg/l Copper in Influent Complexed with Rochelle Salt and EDTA

For these tests, a Precipitator influent was used containing one-fourth the salt concentrations shown in Column II, Table 3. Since this influent composition was reduced to one-fourth of the concentration shown in this table, the influent pH was lower than 8.8-9.0 (i.e. pH 7.6 to 7.8).

1. Tests with 3 Times the FeS Dosage

The first test on this influent stream was run with 3 times the theoretical FeS requirement (about 21 mg/l as FeS), 30 gpm influent rate, pH 8.7 to 8.9, and the mixing zone settleable solids concentration maintained at 18 to 22 volume percent. The results of this test, shown in Figures 7 and 8 for the 23 hour operating period 507

through 530 hours, indicate that these operating conditions are not sufficient to reduce the effluent copper concentration to the desired level (i.e. $\leq$ 0.1 mg/l as Cu). For the first 8 hours of this test, the effluent copper level was within the desired range since it averaged $\leq$0.01 mg/l as Cu during this period. However, after this period, the effluent copper level rose in a 1 hour period to about 0.85 mg/l as copper and then leveled off.

2. Test with 7.8 Times the FeS Dosage

Another test on this influent was run with a higher FeS dosage (i.e. 55 mg/l as FeS or 7.8 times the theoretical FeS dosage). This test is also shown in Figures 7 and 8 for the 23 hour operating period 551 through 574 hours. With the exception of the FeS dose, the operating conditions were maintained as before with 30 gpm influent rate, pH 8.7 to 8.9, and the mixing zone solids concentration maintained at 18 to 25 volume percent.

The results show an effluent copper level lower than the maximum desired level of 0.1 mg/l as copper (i.e. about 0.04 mg/l as Cu).

3. Conclusions

a. Influent complexed copper concentrations in the 5 mg/l as Cu range require higher than 3 times the theoretical FeS requirement. However, the total dosage required is less than the total amount of FeS required for complexed copper influents in the 20 mg/l as Cu range.

b. With the exception of the FeS dosage, the other optimum operating parameters are the same at the 5 mg/l complexed copper level as they are at the 20 mg/l complexed copper level.

c. The sludge blanket in the mixing and settling zones of the Precipitator has a reserve capacity to remove on the order of 0.5 mg/l of complexed copper for 8 hours (at the 30 gpm flow rate) before an increase in the effluent copper occurs. This increase in the effluent copper level is due to an insufficient dosage of fresh FeS over that 8 hour period.

D. Sulfex Precipitator Tests with Influent Containing About 80 mg/l Copper Ion Complexed with Rochelle Salt and EDTA

A Precipitator influent containing about 4 times the salt concentrations shown in Column II, Table 3 was used. The pH of this influent was higher than the 8.8 to 9.0 pH shown in this table. The pH of this more concentrated influent was 9.6 to 9.8, and the lime dose to the FeS slurry tank was lowered in order to maintain the pH in the Precipitator in the 8.5 to 9.0 pH range. Since the concentration of all the constituents in the Column II, Table 3 influent were increased 4 times in going from 20 mg/l Cu to 80 mg/l Cu, the concentrations of the complexing agents were proportionately increased.

1. Test with 2 Times the FeS Dosage

In this test, the average FeS dosage to the Precipitator was maintained at about 225 to 230 mg/l as FeS (i.e. about 2 times theoretical). The other operating conditions were maintained at 30 gpm flow rate, pH 8.7 to 8.9, and the mixing zone settleable solids concentration at 23 to 25 volume percent. The results of this test, shown in Figures 7 and 8 for the 20 hour operating period between 530 and 550 hours, indicate that a higher FeS dosage is necessary because the residual effluent copper levels are high, 1.0 to 1.5 mg/l as Cu.

2. Test with 3 Times the FeS Dosage

The FeS dosage was then increased to 3-3.2 times the theoretical requirement for the influent containing about 80 mg/l of complexed copper. Again, the influent flow rate was maintained at 30 gpm, the pH at 8.8 to 8.9, and the mixing zone settleable solids concentration above 15 volume percent (i.e. 17 to 24 volume percent). Figure 7 shows these test conditions and Figure 8 shows the results for the 21 hour operating period between 574 and 595 hours. The effluent residual copper level is maintained below 0.1 mg/l as Cu during this period.

In both test periods where the influent copper levels averaged about 80 mg/l as copper, the effluent iron levels are high (2 to 8.5 mg/l as Fe) even though the influent dissolved iron levels are still relatively low (0.5 mg/l). This condition is different than in the tests where high effluent iron levels resulted from high influent dissolved iron levels (50 mg/l as Fe). In the

previous tests with low iron influents, the iron added to the process as FeS was removed at pH 8.5 to 9.0. In this test (with low iron and high copper influent), the high iron residuals in the effluent have to be due to the addition of high concentrations of FeS to the influent. The reason for the high iron residuals is probably due to the fact that the very high concentrations of complexing agents (508 mg/l Rochelle salt and 180 mg/l EDTA) have more influence on complexing the soluble iron than they do at one-fourth these concentrations.

3. Conclusions of Sulfex Tests with 80 mg/l of Complexed Copper in the Influent

a. The ferrous sulfide dosage has to be maintained at about 3 times theoretical with the higher influent copper levels.

b. High influent complexed copper levels can be removed as easily as low influent copper levels in the Precipitator provided the FeS dosage and other conditions are maintained at optimum levels.

c. Very high concentrations of complexing agents will interfere with complete precipitation of ferrous hydroxide more strongly than the precipitation of cupric sulfide. The filtered effluents from Sulfex that contain high iron residuals due to the presence of high concentrations of strong complexing agents will have to be treated by oxidation and a second filter or at higher pH values during the sulfide precipitation process (i.e. maintain Precipitator at pH 10.0 to 10.5 or higher). This last alternative (high pH in the Precipitator) would not be desirable when chrome is to be removed.

E. Sulfex Tests with Influent Containing Copper, Cadmium, Chromium, Nickel, and Zinc Complexed with EDTA and Rochelle Salt

In these tests, the five heavy metals were dissolved in the influent at levels of about 4 mg/l each. The composition of this influent is listed in Column III, Table 3. The Precipitator was initially operated with no metals added to the influent for about 16 hours. The purpose of this was to build up a concentration of fresh FeS solids in the mixing zone to bring it to at least 15 volume percent solids before adding the heavy metals.

1. Test with 3.9 Times FeS Dosage

a. Test Conditions

In this test, the Precipitator was operated at a 30 gpm influent rate with 83 mg/l FeS dosage. The theoretical (stoichiometric) requirement for this solution which contains 4 mg/l of each of these five metals is only 21 mg/l of FeS. This requirement is based only on the presence of copper, cadmium, nickel, and zinc (4 mg/l of each). The sulfide of chromium does not occur in aqueous solutions, but chromium does precipitate as the hydroxide of chrome III and does not consume FeS (unless chrome VI is present which is reduced to chrome III by FeS). Therefore, three times the theoretical FeS for these 5 metals, at the concentrations present in the influent, is actually 3 x 21 mg/l or 63 mg/l FeS. The 83 mg/l FeS dose is equal to 3.9 times the theoretical requirement. The pH in the Precipitator was maintained between 8.8 and 9.1, and the solids concentration in the mixing zone was maintained between 17 and 23 volume percent settleable solids.

b. Results

After about 24 hours of operation, the effluent metal concentrations leveled out. The effluent metal concentrations obtained at these steady state conditions are shown in Column A, Table 9. These test conditions and results are shown in Figures 9 and 10 for the 22 hour operating period between 617 and 639 hours. It was apparent from these results that the complexing agents interfered with the removal of most of these metals more than they interfered with the removal of copper. Therefore, it was decided to try a test with an increased sulfide dosage.

2. Test with 5.5 Times the FeS Dosage

a. Test Conditions

The test conditions were maintained as before except for increasing the FeS dosage. The Precipitator was operated at 30 gpm influent rate with 5.5 times the theoretical FeS requirement (117 mg/l as FeS), and the pH was maintained at about 8.8 during this period. The mixing zone solids concentration was maintained between 20 and 30 volume percent during this period.

Table 9. EFFLUENT METAL RESIDUALS FROM PRECIPITATOR TESTS WITH COPPER, CADMIUM, CHROMIUM (III), NICKEL, AND ZINC IN INFLUENT. FOUR MG/L OF EACH METAL PRESENT

Influent Tested	A. Sulfex Test With EDTA and Rochelle Salt (Col. III Table 3)	B. Sulfex Test With Only Rochelle Salt (Col. IV Table 3)	C. Hydroxide Test With Only Rochelle Salt (Col. IV Table 3)
Metal		Effluent Level (mg/l)	
Copper	0.22	0.01	1.5
Cadmium	1.6	<0.01	1.7
Chromium (III)	3.4	3.5	2.0
Nickel	3.6	≤0.4	3.0
Zinc	0.87	≤0.03	1.0
Iron	0.42	≤0.2	--*

*No iron was added to the hydroxide test influent

b. Results

The results obtained are shown in Figure 10 for the 7 hour operating period between 639 and 646 hours. After 6 to 8 hours of running, the effluent residual copper level is significantly reduced from 0.22 mg/l Cu (at 3.9 x FeS dosage) to 0.14 mg/l Cu (at 5.5 x FeS dosage). However, the other heavy metals do not show a significant reduction in their residual effluent concentrations during this same period of time. This test was terminated in order to conduct jar tests to determine the influence of the individual complexing agents on the heavy metals. The results of these tests have already been discussed and are shown in Table 5.

F. Tests with Cu, Cd, Cr(III), Ni, and Zn Complexed with Only Rochelle Salt (Tartrate)

1. Precipitator Test with Sulfex Process

a. Influent Compositions

The composition of the influent for these tests is shown in Column IV, Table 3. This influent had the same concentration of Rochelle salt (126.9 mg/l) as the initial Precipitator tests, but the EDTA was left out because of the jar tests indicated that EDTA forms stronger complexes with most of these metals than does Rochelle salt. Before introducing this influent into the Precipitator, the Precipitator was run with only copper and Rochelle salt in the influent for about 24 hours in order to build a sludge blanket. The old sludge blanket, produced during operation with EDTA in the influent, was disposed of in order to insure formation of a sludge blanket representative of the new influent conditions.

b. Test Conditions

The Precipitator was operated at 30 gpm influent rate with about 3 times the theoretical FeS requirement for 20 mg/l copper (i.e. 80 to 90 mg/l as FeS). During the test period, the pH range was maintained at 8.5 to 9.0 while the solids concentration in the mixing zone was maintained between 22 and 35 volume percent settleable solids.

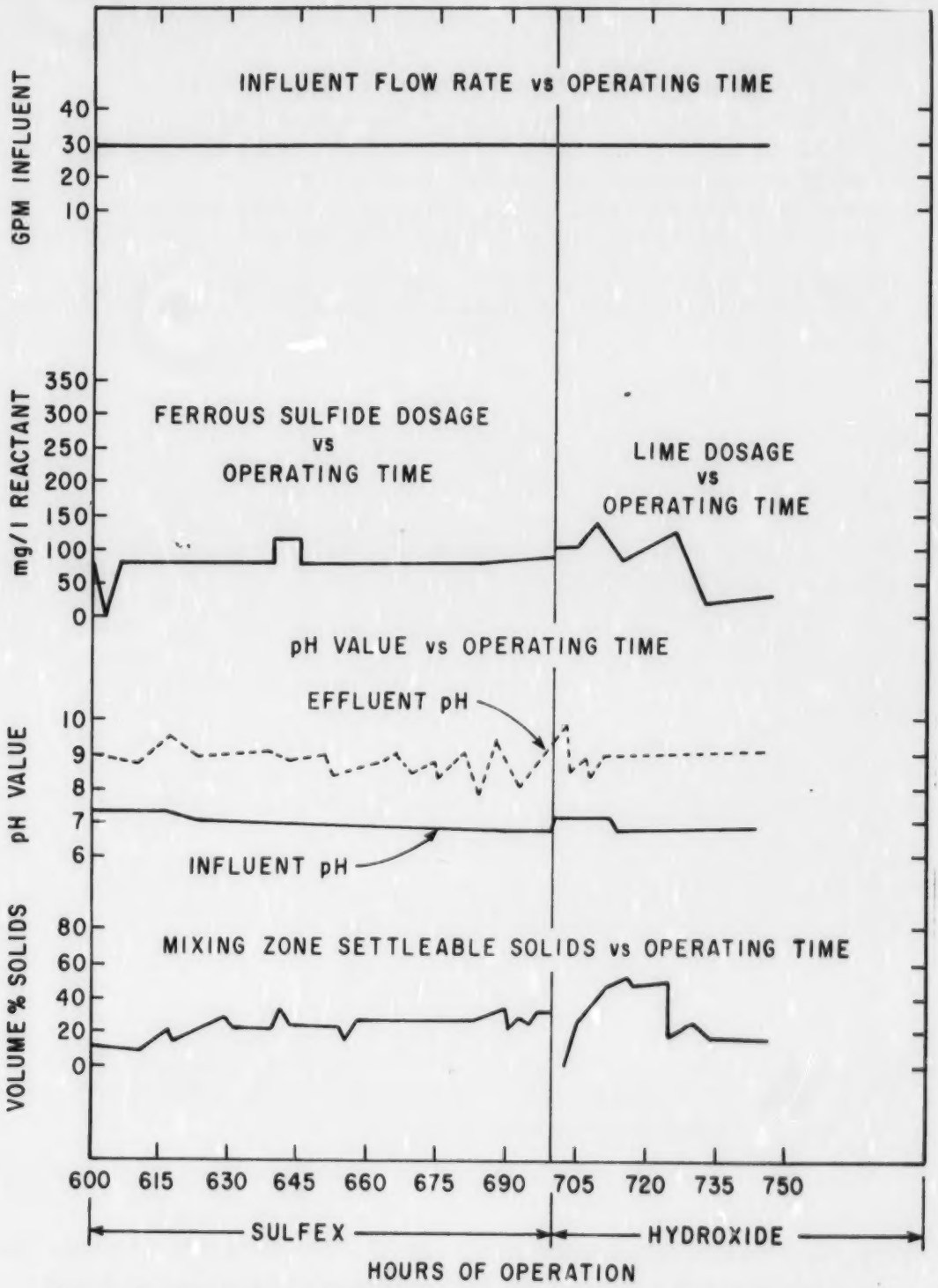


Figure 9. Precipitator operating data for removal of complexed Cu, Cd, Cr, Ni and Zn (from influent containing 4 mg/l of each metal).

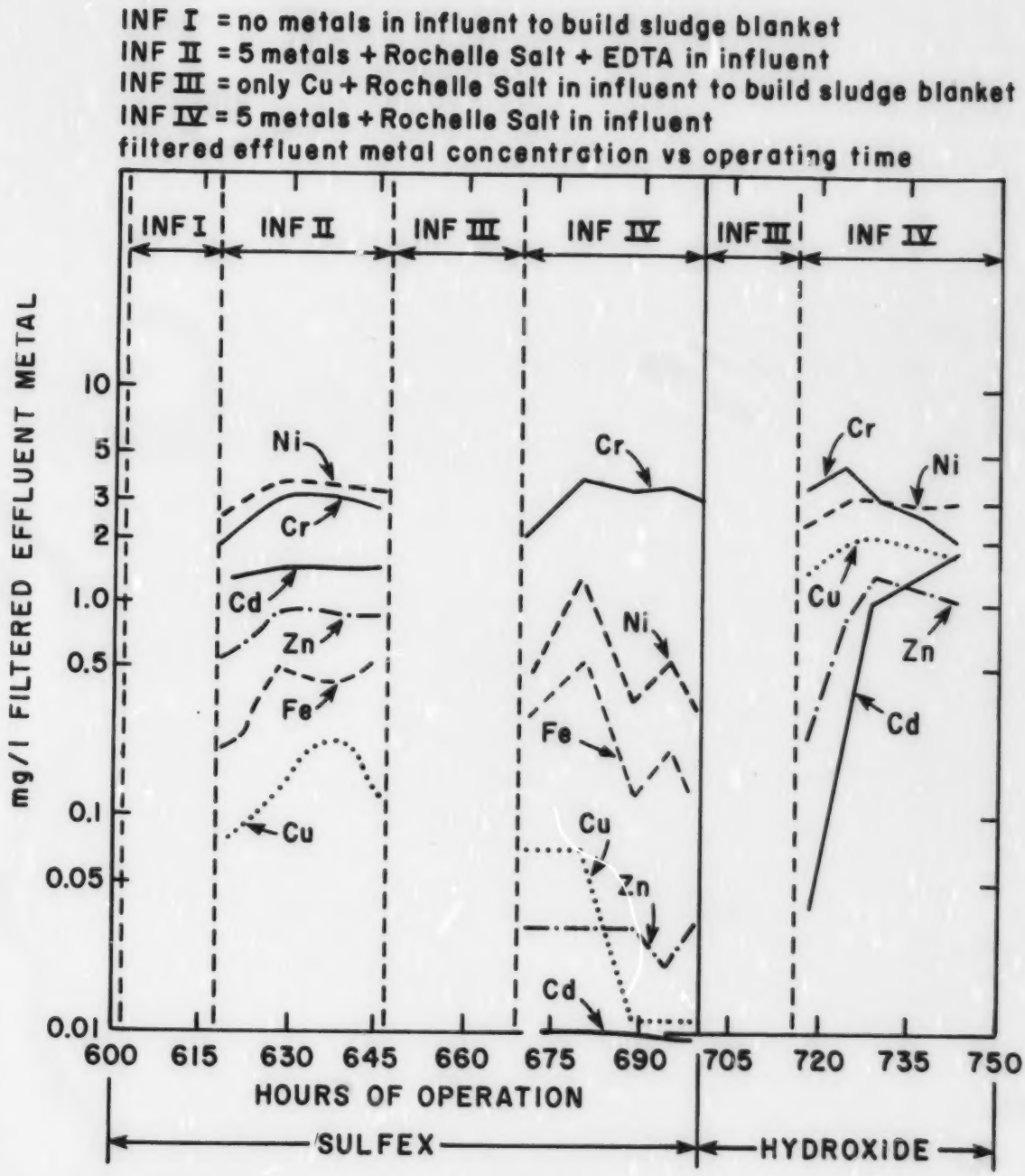


Figure 10. Precipitator operating results for removal of complexed Cu, Cd, Cr, Ni and Zn (from influent containing 4 mg/l of each metal).

c. Results

The conditions and results of this test are shown in Figures 9 and 10 for the 30 hour operating period between 669 and 799 hours. When the quality of the filtered Precipitator effluent reaches constant levels under the given conditions, the effluent concentrations shown in Column B, Table 9 are obtained.

Comparing the results in Column B, Table 9 with those in Column A, Table 9, it is seen that the Rochelle salt is a weaker complexing agent for copper, cadmium, nickel, zinc, and iron than is the EDTA-Rochelle salt combination because better metal removal generally occurred in the solution containing only Rochelle salt. On the other hand, it is seen that chromium is complexed at least as much if not more strongly by Rochelle salt (tartrate) than it is by EDTA. It is reasonable to assume that of the metals tested, the chromium precipitation is most influenced by the Rochelle salt because its removal is accomplished only by hydroxide precipitation. The other metals are more readily precipitated as the sulfides which are much less soluble than the hydroxide species of these metals. Since the tartrate, by forming metal tartrate complexes, tends to be particularly strong in inhibiting the precipitation of metal hydroxide, the metals which can precipitate as sulfides are less influenced by its presence.

2. Precipitator Test with Hydroxide Precipitation

The object of this test was to determine the effectiveness of removal of the 5 metals by precipitation as hydroxides in a single stage precipitation process.

a. Influent Composition

The influent composition in this test was the same as that used in the previous Precipitator test with Sulfex (i.e. Column IV, Table 3). No EDTA was contained in this influent. Using the same influent in the hydroxide process and the Sulfex process tests, a direct comparison was made between the effectiveness of both processes for the removal of Cu, Cd, Cr, Ni, and Zn when a complexing agent (tartrate) is present.

b. Test Conditions

Except that no ferrous sulfide was added to the influent, the Precipitator was operated at the same conditions for the hydroxide precipitation test as for the Sulfex test. The Precipitator was operated at a 30 gpm influent rate and the pH was controlled at about pH 9-9.2 by adding a slurry of hydrated lime, $Ca(OH)_2$, to the influent via a metering pump. The pH value of the hydroxide process was controlled near pH 9.0 for the following reasons:

(1) The pH value where the solubility of the hydroxides of these five metals is at a minimum is different for each metal. For copper, cadmium, and nickel, the solubility decreases with increasing pH. The higher the pH, the lower the residual metal concentrations will be (i.e. pH should be 9.0 or higher for best results). Chrome III and zinc hydroxides are amphoteric. The minimum solubilities are obtained within rather narrow pH ranges. The pH ranges of minimum solubilities for Cr and Zn differ somewhat in the literature because the composition of the solution containing these metals has an influence on the solubilities. Generally, the most appropriate theoretical pH range to achieve the lowest possible solubilities of these metal hydroxides, in treatment of most squeous solutions, would be about pH 9. The EPA seminar publication Waste Treatment (Upgrading Metal-Finishing Facilities to Reduce Pollution)[6] shows the solubilities of these metal hydroxides at different pH values and how they can vary from one source to another.

(2) The regulations on the maximum permissible pH values for waste disposal are generally about 9.5; therefore, higher pH values would usually require a subsequent neutralization step after filtration.

REFERENCES

6. Lancy, L. E. and R. L. Rice, Upgrading Metal-Finishing Facilities to Reduce Pollution: Waste Treatment, Environmental Protection Agency, Technology Transfer Seminar Publication No. 2, Fuly 1973, pp. 28-30

(3) Common practice in the treatment of metal finishing wastes (containing these metals) by hydroxide precipitation is to operate somewhere in the pH 8.0 to 9.0 range.

In addition to the reasons listed above for operating our test at pH 9.0, this test gave us the opportunity to compare Sulfex with hydroxide precipitation in the same approximate pH range. The same polyelectrolyte used in the Sulfex tests was added to the hydroxide test at about the same concentration (4 mg/l). The hydroxide test Precipitator effluent was polished by the same dual media sand anthracite filter that was used in the Sulfex tests. Before adding the 5 metals to the influent, the Precipitator was run with a copper containing influent for about 16 hours to build up an adequate sludge blanket. The solids concentration in the mixing zone was maintained at 18 to 22 volume percent during the actual test with the 5 metals.

c. Results

The conditions and results of this test are shown in Figures 9 and 10 for the 27 hour operating period between 717 and 744 hours. When the filtered Precipitator effluent quality reaches equilibrium, the average metal concentrations shown in Column C, Table 9 are obtained.

C. Conclusion of Precipitator Tests with Cu, Cd, Cr, Ni, and Zn in the Influent

1. EDTA interferes with the precipitation of the 5 metals in the Sulfex Process more severely than the Rochelle salt.

2. EDTA hinders the precipitation of cadmium and nickel more than it does copper, chromium, zinc, and iron with the Sulfex Process.

3. With Rochelle salt present, but no EDTA, about 3-4 times the theoretical requirement of FeS removed the metals to or below the maximum desired levels for all metals except chromium which was not removed effectively.

4. When Rochelle salt is present, the trivalent chromium is not effectively removed because chromium III is only removed as the hydroxide. The optimum pH range for lowest $Cr(OH)_3$ solubility is in the 8 to 9.0 range. The presence of hydroxyl ion enhances the formation of the Cr-tartrate complexes that hinders the formation of $Cr(OH)_3$.

5. As expected, in the presence of a complexing agent such as tartrate, Sulfex is significantly more effective in removing the metals than conventional lime (hydroxide) treatment.

6. Chromium III is not removed any more effectively in the Sulfex process than in the hydroxide process. However, in cases where Chrome VI is to be removed, Sulfex can reduce the Cr^{+6} to Cr^{+3} and remove it in one step. Therefore, for the removal of total chrome, the Sulfex process is superior to the conventional hydroxide process.

7. Further studies are necessary to evaluate Sulfex on actual electroplating plant effluents where various other complexing agents (and other compounds) are present at various levels of concentration.

SECTION VI

DCG (SLUDGE DEWATERING) TESTS

A. Laboratory Sludge Dewatering Tests

1. Description of Laboratory Sludge Dewatering Tests

The settled sludges from the Sulfex jar tests and the initial Sulfex Precipitator tests were saved and used as samples for the laboratory sludge dewatering tests. These small scale tests are routinely performed to predict the operating conditions and operating results of Permutit's Dual Cell Gravity Filter (DCG) and Multi Roller Press (MRP). The tests consist of a simulated rapid mixing step in which the best type and dose of polyelectrolyte, needed to condition the sludge, is determined. The operation of the DCG is then simulated using the conditioned sludge as feed for a bench top roll test. This test provides information on the percent solids in the dewatered cake (sludge roll) and on the suspended solids in the subnatant (water drained from sludge). Following simulated DCG operation, the MRP is simulated by a simple sludge pressing test in order to give a rough estimate of the percent solids in the further dewatered cake that results from Multi Roller Press operation.

2. Results of the Laboratory Sludge Dewatering Tests

The laboratory dewatering tests were made on Sulfex sludges of about 1.0 weight percent solids. These tests show that either cationic or mild anionic polyacrylamide polyelectrolytes condition the sludges satisfactorily. The following results are obtainable:

a. DCG test cake = 5 weight percent solids

b. MRP test cake = 8 weight percent solids

c. Polyelectrolyte requirement = 100 to 150 mg/l of a cationic polyacrylamide

d. Consistency of MRP cake is that of a bladeable material

In the actual pilot plant tests, the DCG was fed sludge from a decanting tank in which the solids concentration of the Precipitator blowoff sludge was increased from 1.0 weight percent to over 3 weight percent solids. As a result, the DCG and MRP cakes obtained had a higher solids concentration than the laboratory tests predicted. The results of the pilot plant dewatering tests are discussed below (Section IV, Part B, "Full Scale DCG-MRP Tests").

B. Full Scale DCG and MRP Tests

1. Objective

The full scale Dual Cell Gravity Filter (DCG) and Multi Roller Press (MRP) units were run in combination. These tests were made to determine the effectiveness and operating requirements for a full-scale DCG-MRP sludge dewatering plant.

2. Operating Procedure

The 1.0 to 1.5 weight percent blowdown sludge from the Precipitator operation was collected in a decanting tank of about 1500 gallons total capacity. The Precipitator blowdown rate was approximately 0.5 to 1.0 gpm at the 30 gpm influent rate and the sludge was removed intermittently. During periods of no blowdown, especially at night, a high degree of settling took place and it was possible to decant the supernatant liquor. After about 2 weeks of operation, the settled sludge level was such that the decanting tank could not accept more Precipitator blowdown sludge without solids escaping in the overflow. The volume of decanted sludge was then about 1000 gallons. When the decanted sludge reached this level, the clear water on top of the settled sludge was siphoned off. When, the sludge in the tank was agitated with a mechanical agitator to evenly distribute the solids in the holding tank so that a homogeneous sludge was fed to the DCG via a sludge pump. The concentration of this sludge was about 3 to 3.5 weight percent solids. The 1000 gallons of sludge could be dewatered by the DCG-MRP combination within 4 to 6 hour periods which includes time needed for homogenizing of the holding tank sludge and start up of the dewatering equipment. A high molecular weight slightly anionic polyacrylamide sludge conditioner was mixed with the DCG influent (in a separate mixing tank) before it entered the DCG. See Section III b for additional description of the assembly and operation of the Precipitator pilot plant.

3. Results of the Full Scale Dewatering Tests

a. The sludge from the holding tank is a very thick but still fluidized 3 to 3.5 weight percent. This sludge is pumped to the DCG at about 5 gpm. An average polyelectrolyte concentration of 125 to 150 mg/l is necessary to condition the sludge prior to the DCG.

b. When the treated sludge passes through the DCG, the sludge solids concentration increases to about 14 to 15 weight percent.

c. The sludge cake from the DCG is immediately conveyed to the MRP where more water is pressed out leaving a sludge containing about 26 weight percent solids. This final sludge has a bladeable dryness that is suitable for final disposal.

d. On the basis of the final sludge from the MRP, the polyelectrolyte requirement is calculated at 7.7 pounds of polymer per ton of dry solids.

e. The standard DCG units have speed controls for varying the rotation speed of the DCG screen which enables operation at higher influent rates. The DCG unit used in this test did not have a speed control. It is estimated that the sludge can be dewatered at a rate of about 7 gpm in the same size unit equipped with a speed control.

4. Conclusions

Dewatering the sludge from the Sulfex process to a bladeable solid can be routinely accomplished by conventional sludge dewatering operations.

SECTION VII

COST ESTIMATES

A. Chemical Operating Costs

A comparison of the estimated chemical operating costs for the hydroxide and Sulfex processes is shown in Tables 10 and 11. Table 10 shows the difference between the chemical costs of hydroxide and Sulfex for wastes containing various concentrations of copper. In each case, the copper is complexed with tartrate and EDTA. This table shows that, although conventional hydroxide treatment (pH 9) chemical costs are lower than Sulfex costs, the effluent quality obtained does not meet the EPA standards. Improved copper removal is obtained by hydroxide precipitation at very high pH (12), which raises the chemical costs to considerably more than Sulfex, but the effluent quality is still not good enough to meet the EPA standards. Table 10 also shows that although the EPA standards are met with Sulfex at about neutral pH (7.5), it is less costly to obtain even better effluent quality by operating at pH values of about 8.5. The reason for this is that the required dosage of ferrous sulfide reactant is less at higher pH value.

Table 11 shows the difference between chemical costs of hydroxide and Sulfex for wastes containing mixtures of common heavy metals in both complexed and uncomplexed solutions. Waste composition a in Table 11 contains a mixture of five common heavy metals complexed with tartrate (Rochelle salt). At pH 9 hydroxide precipitation is less costly, but the residual metals obtained in the effluent at this pH are all higher than the EPA standards. Even operation at pH 12, which adds high chemical costs due to the additional lime required plus the acid for neutralization, does not meet the EPA standard for copper. Sulfex, however, removed all the metals, except chromium, to levels below the EPA standards at a pH value within the EPA standards for waste disposal.

A comparison between hydroxide precipitation and Sulfex is shown for jar tests made on waste composition b in Table 11. These jar tests show that the uncomplexed combination of metals in solution are reduced to meet the EPA standards by Sulfex or, at pH 10, by lime. However, the cost of hydroxide at pH 10 is about the same as Sulfex which gives equal or better effluent quality. Also, the hydroxide process at pH 10 has the disadvantage of requiring a final acidification step after filtration in order to meet the EPA standard of pH 6.0 to 9.5 for discharge.

Table 10. CHEMICAL COSTS OF HYDROXIDE VS. SULFEX FOR VARIOUS COPPER CONCENTRATIONS

Waste Composition	Effluent Quality (mg/l Cu)	pH	Process	Cost ¢/1000 Gal.
a. 5 mg/l Cu complexed with Tartrate & EDTA	<0.10	8.5	Sulfex	8.8
	<0.25	7.5	Sulfex	9.5
	*EPA 0.5	6.0-9.5	-	-
	1.5	12	Hydroxide	31.8
	≥4.3	9	Hydroxide	2.4
b. 20 mg/l Cu complexed with Tartrate & EDTA	<0.1	8.5	Sulfex	13.1
	<0.25	7.5	Sulfex	15.8
	*EPA 0.5	6.0-9.5	-	-
	4.3	12	Hydroxide	32.1
	12	9	Hydroxide	2.7
c. 80 mg/l Cu complexed with Tartrate & EDTA	<0.10	8.5	Sulfex	45.6
	<0.25	7.5	Sulfex	57.6
	*EPA 0.5	6.0-9.5	-	-
	≥4.3	12	Hydroxide	33.9
	≥12	9	Hydroxide	4.8

* Maximum daily average allowed by EPA. Based on rinse water usage of 160 l/sq. meter for existing plants electroplating common metals according to 4-24-75 Federal Register.

Table 11. CHEMICAL COSTS OF HYDROXIDE VS. SULFEX FOR WASTES CONTAINING MIXTURES OF COMMON HEAVY METALS

Waste Composition	Effluent Quality (mg/l) Cu	Cd	Cr^{+3}	Ni	Zn	pH	Process	Cost ¢/1000 Gal.
a. Tartrate Complexed Cu, Cd, Cr^{+3}, Ni, and Zn at 4 mg/l Each	<0.1	0.01	3.2	0.4	<0.05	8.5	Sulfex	14
	*EPA 0.5	0.3	0.5	0.5	0.5	6.0-9.5	-	-
	0.05	0.05	<0.1	<0.1	0.17	12	Hydroxide	32.8
	1.2	1.7	2.0	3.0	1.0	9	Hydroxide	3.6
b. Uncomplexed Cu, Cd, Cr^{+3}, Ni, and Zn at 4 mg/l Each	0.01	0.1	<0.05	0.05	0.01	8.5	Sulfex	6.5
	<0.1	<0.1	<0.1	<0.1	<0.1	10	Hydroxide	7.2
	*EPA 0.5	0.3	0.5	0.5	0.5	6.0-9.5	-	-
	0.1	3.8	<0.5	2.3	1.3	7.5	Hydroxide	2.4
c. **25 mg/l Cr^{+6} 6 mg/l Zn			Cr^{+6}	Zn				
			<0.05	0.1		8.5	Sulfex	12.2
		*EPA	0.05	0.5		6.0-9.5	-	-
			<0.05	0.8		8.5	Hydroxide	17.4

* Maximum daily average limitations for existing plants electroplating common metals. Based on rinse water usage of 160 l/sq. meter according to 4-25-75 Federal Register.

** Waste composition c. is an Actual Waste Water from manufacture of automotive parts.

The results shown for hydroxide effluent quality at pH 10 on waste composition b is actually lower than the theoretical solubilities for the hydroxides of cadmium, chromium, nickel, and zinc. It is assumed that these better than expected results are due to co-precipitation and/or other interactions of the metal hydroxides. Therefore, it should not be concluded that hydroxide precipitation can always reduce these metals to the values shown in Table 11 at pH 10, since the combinations of metals present in the influent waste can change frequently. The results obtained for Sulfex, shown in Table 11 at pH 8.5 for waste composition b, are well above the theoretical solubilities and do not depend on the presence of several different metals to meet the EPA standards. Therefore, for a combined metal influent without complexing agents, the Sulfex process is more predictable than hydroxide precipitation with respect to effluent quality.

Waste composition c shown in Table 11 is an actual plant waste that was studied in jar tests. In order to reduce the hexavalent chromium to permissible levels, by EPA standards, the chrome $^{+6}$ was reduced by sulfite reduction at low pH before hydroxide precipitation at pH 9.5 was used. The zinc is not removed to the required level with hydroxide precipitation in this case. Sulfex reduces the Cr^{+6} and precipitates the Cr^{+3} in the same step while simultaneously removing the zinc to below the maximum permissible level. The chemical cost is less for Sulfex than hydroxide precipitation in this case. A detailed breakdown of the chemical costs shown in Tables 10 and 11 is presented next. These cost estimates are based on the chemical requirements for the optimum conditions found during the Sulfex studies.

Breakdown of Chemical Costs

The chemical prices used in the following cost estimates are averages for the high and low values listed in the Oil, Paint and Drug Reporter[7] for July 28, 1975. The chemical cost for NaHS should be increased by 56.6 percent if 45 percent liquid NaHS is used instead of the 71 percent flake NaHS shown in these estimates. The cost for sulfuric acid at 5¢ per pound is based on purchasing 55 gallon drum lots instead of bulk basis or carboys which varies the price from 2¢ to 8¢ per pound.

REFERENCES

7. Chemical Marketing Reporter. Oil, Paint and Drug Reporter. Schuell Publishing Company, Inc., July 28, 1975.

1. Chemical Operating Cost for Influent Containing Copper Complexed with Tartrate and EDTA

a. Influent containing 5 mg/l complexed copper

(1) Hydroxide Process

Eff. Qual. (mg/l Cu)		Chemical	Dosage lb/1000 gal.		Cost	Cost ¢/1000 gal.	
pH 9	pH 12		pH 9	pH 12	¢/lb	pH 9	pH 12
≤4.3	1.5	$Ca(OH)_2$	0.5	4.6	1.8	0.9	8.3
		Polymer	0.025	0.025	60	1.5	1.5
		H_2SO_4	-	4.4	5	-	22.0
					Total	2.4	31.8

(2) Sulfex Process

Eff. Qual. (mg/l Cu)		Chemical	Dosage lb/1000 gal.		Cost	Cost ¢/1000 gal.	
pH 7.5	pH 8.5		pH 7.5	pH 8.5	¢/lb	pH 7.5	pH 8.5
<0.25	<0.1	71% NaHS	0.19	0.17	11.25	2.1	1.9
		$FeSO_4 \cdot 7H_2O$	1.58	1.38	2.25	3.6	3.1
		Polymer	0.03	0.03	60.00	1.8	1.8
		$Ca(OH)_2$	1.13	1.13	1.80	2.0	2.0
					Total	9.5	8.8

b. Influent containing 20 mg/l complexed copper

(1) Hydroxide Process

Eff. Qual. (mg/l Cu)		Chemical	Dosage lb/1000 gal.		Cost		
						¢/1000 gal.	
pH 9	pH 12		pH 9	pH 12	¢/lb	pH 9	pH 12
12	4.3	$Ca(OH)_2$	0.5	4.6	1.8	0.9	8.3
		Polymer	0.03	0.03	60	1.8	1.8
		H_2SO_4	-	4.4	5	-	22.0
					Total	2.7	32.1

(2) Sulfex Process

Eff. Qual. (mg/l Cu)		Chemical	Dosage lb/1000 gal.		Cost		
						¢/1000 gal.	
pH 7.5	pH 8.5		pH 7.5	pH 8.5	¢/lb	pH 7.5	pH 8.5
0.25	0.1	71% NaHS	0.37	0.28	11.25	4.2	3.2
		$FeSO_4 \cdot 7H_2O$	3.07	2.30	2.25	6.9	5.2
		Polymer	0.04	0.04	60	2.4	2.4
		$Ca(OH)_2$	1.3	1.3	1.8	2.3	2.3
					Total	15.8	13.1

c. Influent containing 80 mg/l complexed copper

(1) Hydroxide Process

Eff. Qual. (mg/l Cu)		Chemical	Dosage lb/1000 gal.		Cost	Cost ¢/1000 gal.	
pH 9	pH 12		pH 9	pH 12	¢/lb	pH 9	pH 12
≥12	≥4.3	$Ca(OH)_2$	0.67	4.6	1.8	1.2	8.3
		Polymer	0.06	0.06	60	3.6	3.6
		H_2SO_4	-	4.4	5	-	22.0
					Total	4.8	33.9

(2) Sulfex Process

Eff. Qual. (mg/l Cu)		Chemical	Dosage lb/1000 gal.		Cost	Cost ¢/1000 gal.	
pH 7.5	pH 8.5		pH 7.5	pH 8.5	¢/lb	pH 7.5	pH 8.5
<0.25	<0.1	71% NaHS	1.4	1.1	11.25	15.8	12.4
		$FeSO_4 \cdot 7H_2O$	12	9.2	2.25	27.0	20.7
		Polymer	0.06	0.05	60	3.6	3.0
		$Ca(OH)_2$	6.2	5.3	1.8	11.2	9.5
					Total	57.6	45.6

2. Chemical Operating Cost for Influents Containing Mixtures of Common Heavy Metals

a. Influent containing 4 mg/l each of Cu, Cd, Cr^{+3}, Ni, and Zn complexed with Rochelle salt

The required FeS dosage was the same for this influent as for the one containing 20 mg/l of copper complexed with EDTA and Rochelle salt. However, due to the higher pH of the 20 mg/l complexed copper influent, the lime requirement was higher for this influent which had a lower initial pH (i.e. pH 6.8 instead of pH 8 to 9).

(1) Hydroxide Process

	Eff. Qual. (mg/l)		Chemical	Dosage lb/1000 gal.		Cost	¢/1000 gal.	
	pH 9	pH 12		pH 9	pH 12	¢/lb	pH 9	pH 12
Cu	1.2	0.65	$Ca(OH)_2$	1.0	5.0	1.8	1.8	9.0
Cd	1.7	0.05	Polymer	0.03	0.03	60	1.8	1.8
Cr	2.0	<0.1	H_2SO_4	-	4.4	5	-	22.0
Ni	3.0	<0.1						
Zn	1.0	0.17				Total	3.6	32.8

(2) Sulfex Process

	Eff. Qual. (mg/l)	Chemical	Dosage lb/1000 gal.	Cost ¢/1000 gal.	
	pH 8.5		pH 8.5	¢/lb	pH 8.5
Cu	<0.1	71% NaHS	0.28	11.25	3.2
Cd	0.01	$FeSO_4 \cdot 7H_2O$	2.3	2.25	5.2
Cr	3.2	Polymer	0.04	60	2.4
Ni	0.4	$Ca(OH)_2$	1.8	1.8	3.2
Zn	<0.05				
				Total	14.0

b. Influent containing 4 mg/l each of Cu, Cd, Cr^{+3}, Ni, and Zn without complexing agents

The following chemical costs are based on studies using jar tests with synthetic wastes to compare hydroxide precipitation with Sulfex. The pH of the influent used in these tests was about pH 6.0.

(1) Hydroxide Process

	Eff. Qual. (mg/l)		Chemical	Dosage lb/1000 gal.		Cost ¢/1000 gal.		
	pH 7.5	pH 10		pH 7.5	pH 10	¢/lb	pH 7.5	pH 10
Cu	0.1	<0.1	$Ca(OH)_2$	0.33	0.92	1.8	0.6	1.7
Cd	3.8	<0.1	Polymer	0.03	0.03	60	1.8	2.4
Cr	<0.5	<0.1	H_2SO_4	-	0.61	5	-	3.1
Ni	2.3	<0.1						
Zn	1.3	<0.1				Total	2.4	7.2

(2) Sulfex Process

	Eff. Qual. (mg/l)	Chemical	Dosage lb/1000 gal.	Cost ¢/1000 gal.	
	pH 8.5		pH 8.5	¢/lb	pH 8.5
Cu	0.01	71% NaHS	0.09	11.25	1.0
Cd	0.1	$FeSO_4 \cdot 7H_2O$	0.77	2.25	1.7
Cr	<0.05	Polymer	0.03	60	1.8
Ni	0.05	$Ca(OH)_2$	1.13	1.8	2.0
Zn	0.01				
				Total	6.5

c. Influent containing 25 mg/l hexavalent chromium and 6 mg/l of zinc

The following chemical costs are based on jar tests with an actual plant waste sample that was assumed to have little or no strong complexing agents present. Sodium bisulfite ($NaHSO_3$) was selected as the reducing agent in the hydroxide process for reasons of safety, availability, and handling.

Process	Eff. Qual. (mg/l)	Chemical	Dosage lb/1000 gal.	¢/lb	¢/1000 gal.
Hydroxide* Step 1	T-Cr <0.05 Zn 0.8	H_2SO_4 (pH 2) + $NaHSO_3$	0.75 0.69	5 12.7	3.8 8.8
Hydroxide* Step 2		$Ca(OH)_2$ (pH 8.5) + Polymer	1.35 0.04	1.8 60	2.4 2.4
				Total	17.4
Sulfex	T-Cr <0.05 Zn 0.1	71% NaHS $FeSO_4 \cdot 7H_2O$ Polymer $Ca(OH)_2$ (pH 8.5)	0.25 2.07 0.04 1.3	11.25 2.25 60 1.8	2.8 4.7 2.4 2.3
				Total	12.2

* The requirements for acid and reducing agent used in these hydroxide tests are based on requirements for hexavalent chrome reduction as shown in the Electroplating Engineering Handbook[5].

3. Chemical Operating Costs for Sludge Dewatering

The following costs are based on the results of running sludge dewatering tests on the Sulfex sludges with the DCG/MRP dewatering system. The amount of sludge resulting from the hydroxide Precipitator tests was not enough to make a full scale evaluation of the chemical requirements.

Chemical	mg/l	¢/lb	lbs/ton dry solids	$/ton dry solids
Polymer	138	200	7.7	15.40

One thousand gallons of Precipitator influent produced about 5 gallons of sludge requiring 138 mg/l of polymer to dewater.

The sludge dewatering chemical operating cost was:

$$0.138\ g/\ell \times \frac{1\ lb}{454g} \times \frac{3.785\ \ell}{gal} \times 5\ gal \times 200¢/lb = 1.15¢/1000\ gal\ of\ Precipitator\ influent$$

Therefore, sludge dewatering will add about 1.15¢/1000 gallons to the above Precipitator chemical operating costs.

B. Capital Equipment Costs for Sulfex

1. Description of System Used as Basis for Equipment Cost

The equipment cost for a Sulfex heavy metal removal system is shown for a 40 gpm plant. The Precipitator is sized to operate at a surface rate of 1.6 gpm/ft^2 of chevron surface area and the filter at a surface rate of 3.2 gpm/ft^2. These capacities are conservative and offer ample safety margin for handling normal shock loads and similar irregularities in the operation of the treatment process. A diagram of this system is shown in Figure 11 and includes the basic equipment involved.

The makeup of the wastewater treated by this system is assumed to have the following average constituent concentrations.

Constituent	mg/l total	mg/l dissolved
Chromium (as Cr)	50	25 (as Cr^{+6})
Zinc (as Zn)	20	6
Copper (as Cu)	5	1
Nickel (as Ni)	1	0.5
Iron (as Fe)	20	1.0
Calcium (as Ca)	20	20
Suspended solids	100	-
pH	6	-

In addition to the heavy metals listed, other heavy metals such as cadmium, lead, mercury, etc. may also be present up to several mg/l of each without changing the equipment costs. The presence of strong complexing agents is assumed to be low or absent.

2. Equipment Cost

a. Installed Cost

The installed cost determined for an actual proposal of the plant shown in Figure 11 is estimated at $130,290. The installation cost includes neutralization tanks constructed below ground level to save space. It is estimated that installation costs for tanks of above ground construction would be substantially lower. For spare chemical feed pumps, sump pump, and transfer pump, $5,000 should be added to the selling price.

b. Selling Price

Equipment	Price
1. Precipitator with clear well, centrifuge for dewatering, chemical feeds and agitators, and engineering drawings	$ 39,126
2. Filter with transfer pump and engineering drawings	4,337
3. Neutralization system including agitators, chemical feeds, pH controls, sump pump, and engineering drawings	49,002
Total selling price	$ 92,465
c. Installation Cost (estimated by outside contractor)	$ 37,825

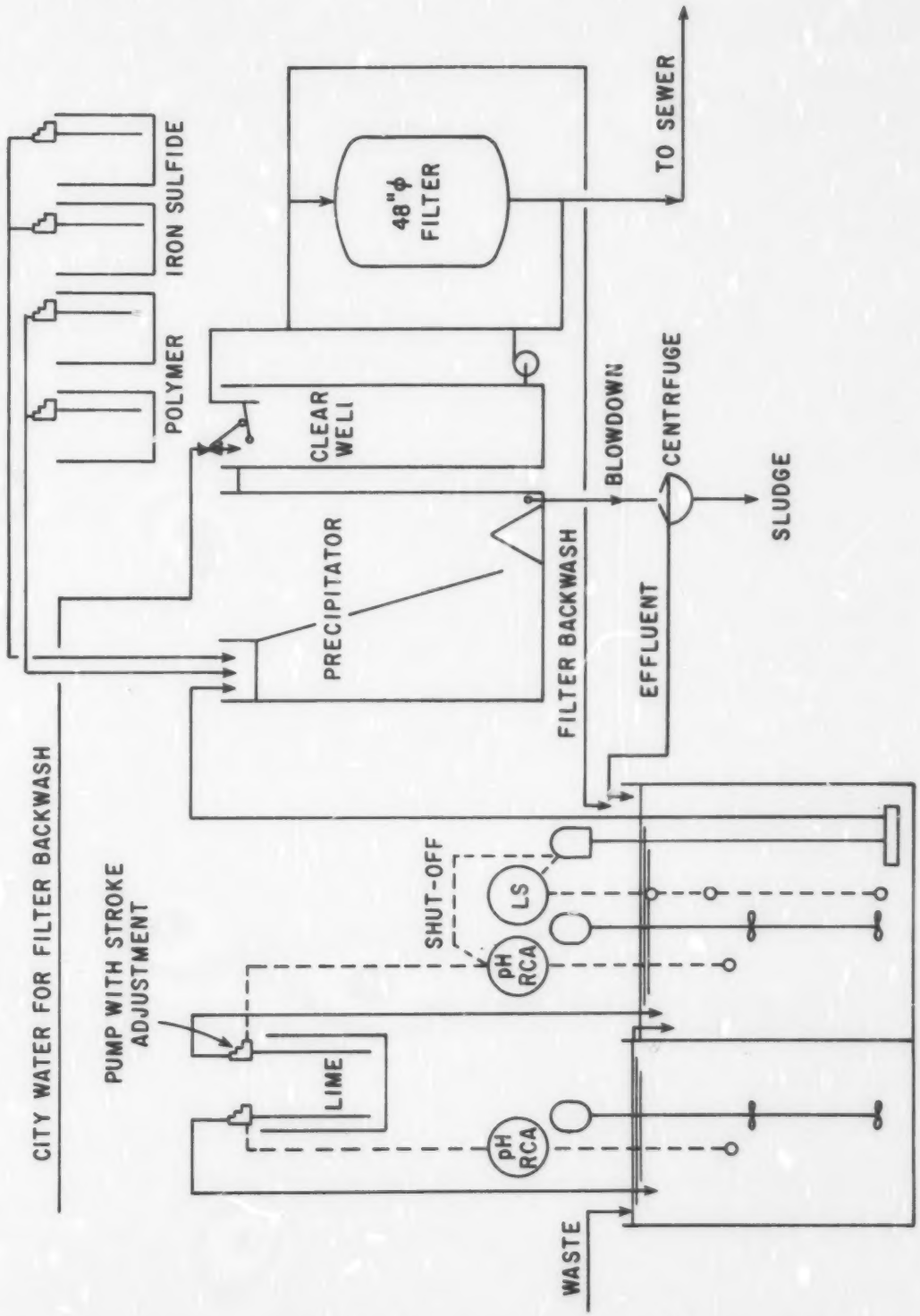


Figure II. 40 GPM Sulfex plant for combined removal of Cr^{+6}, Zn, Cu, Cd, Ni and Fe.

SECTION VIII

REFERENCES

1. Fales, H. A. and F. Kenny. Inorganic Quantitative Analyses. New ed. Appleton Century Co., New York-London, p. 233, 1939.

2. Handbook of Chemistry and Physics, 50th ed., Robert C. Weast, ed. The Chemical Rubber Company, p. B252, 1969.

3. Handbook of Analytical Chemistry, Louis Meites, ed. McGraw-Hill, Inc., pp. 1-15, 1-19, 1963.

4. Metal Finishing Guidebook and Directory for 1970. Nathaniel Hall, ed. Palmer H. Langdon, pub., p. 473, 1970.

5. Ward, A. E., Chapter 11, Wastewater Control and Treatment. In: Electroplating Engineering Handbook, 3rd Ed., Graham, A. K. (ed.), New York, New York, Van Nostrand Reinhold Company, pp. 359-360, 1971.

6. Lancy, L. E. and R. L. Rice. Upgrading Metal Finishing Facilities to Reduce Pollution: Waste Treatment. Environmental Protection Agency Technology Transfer Seminar Publication No. 2, July 1973. U. S. Government Printing Office, pp. 28-30, 1974

7. Chemical Marketing Reporter. Oil, Paint and Drug Reporter. Schnell Publishing Company, Inc., July 28, 1975